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I. Derivatives of the Tetrachlorides of Zirconium, Thorium, and Lead. By J. Merritt Matthews.
II. Derivatives of the Tetrabromides of Zirconium and Thorium. By J. Merritt Matthews.
III. The Preparation of Zirconium Nitrides. By J. Merritt Matthews.
IV. On the Separation of Iron from Zirconium and Certain Other Allied Metals. By J. Merritt Matthews.
Atomic Volume as a Periodic Function. By Thomas Bayley.
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Commercial Iron Silicides with a High Percentage of Silicon; Their Properties, Manufacture, and Uses. By G. de Chalmot.
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VOLUMETRIC APPARATUS.[1]

BY G. E. BARTON.

Received August 19, 1898.

THERE have been various ideas as to what volumetric apparatus should represent, and the subject has been carefully studied in Europe for several years. Several reports have been made by German chemical societies and by committees of the international congresses of applied chemistry which have been held in Brussels and Paris during recent years. The Imperial Bureau of Weights and Measures of Germany has taken up the matter, and has minutely defined the conditions under which it works in testing apparatus submitted for that purpose. A report which I have not seen was submitted at the congress held recently in Vienna.

The various ideas as to what volumetric apparatus should represent may all be brought under the following three types: Apparatus of the first type contains the named volume at the specified temperature; of the second, contains such a volume of water at the specified temperature, that if (disregarding the container) the water were cooled down to 3.93° C., its volume would be the named volume; of the third, contains the same number of grams of pure water free from air when weighed in dry air at the specified temperature and 760 mm. pressure, as the number of cubic centimeters or grams marked upon them.

Table I shows the volume of water contained at the various specified temperatures by liter flasks of these three types, the

[1] Read at the Boston Meeting of the American Chemical Society, August, 1898.

TABLE I.

THE CALCULATED CONTENTS OF LITER FLASKS OF VARIOUS TYPES.

In these calculations it is assumed that the density of the weights is 8.3, that the barometer stands at 760 mm., that the coefficient of cubical expansion of glass is 0.000025, and that 1000 cc. of pure water, free from air, weigh 1000 grams *in vacuo* at 3.93° C.

Type.	Specified temperatures. °C.	= °F.	Volumes contained at the specified temperatures.	Weight in air of water to fill flasks at the specified temperatures.	Volume contained at 22° C.	Weight in air of water contained at 22° C.
			Cc.	Grams.	Cc.	Grams.
I. Contain the named volume at the specified temperatures.....	3.93	39.074	1000.000	998.879	1000.452	997.197
	4.0	39.2	1000.000	998.879	1000.450	997.195
	15.0	59.0	1000.000	998.051	1000.175	996.921
	15.5	59.9	1000.000	997.978	1000.163	996.909
	15.555+	60.0	1000.000	997.967	1000.161	996.907
	16.666+	62.0	1000.000	997.790	1000.133	996.879
	17.5	63.5	1000.000	997.648	1000.113	996.858
	20.0	68.0	1000.000	997.173	1000.050	996.796
	22.0	71.6	1000.000	996.747	1000.000	996.747
II. Contain such a volume of water at the specified temperature that if the water (disregarding the container) were cooled down to 3.93° C. the volume of the water would be the named volume.	15.0	59.0	1000.872	998.921	1001.047	997.790
	15.555+	60.0	1000.958	998.923	1001.119	997.862
	22.0	71.6	1002.206	998.945	1002.206	998.945
III. Contain the same number of grams of pure water, free from air, when weighed at the specified temperature as the number of cubic centimeters or grams named upon them	3.93	39.074	1001.122	1000.000	1001.575	998.316
	4.0	39.2	1001.122	1000.000	1001.573	998.314
	15.0	59.0	1001.953	1000.000	1002.128	998.868
	15.5	59.9	1002.026	1000.000	1002.189	998.928
	15.555+	60.0	1002.037	1000.000	1002.199	998.938
	16.666+	62.0	1002.215	1000.000	1002.348	999.087
	17.5	63.5	1002.357	1000.000	1002.470	999.209
	20.0	68.0	1002.835	1000.000	1002.885	999.622
	22.0	71.6	1003.264	1000.000	1003.264	1000.000

weight of water which they would contain at the specified temperature, the volume which they would contain when at 22° C., and the weight which they would contain at 22° C. In this table appear temperatures that have never got much, if any, beyond being proposed. 3.93° C. is the temperature at which a liter of water is assumed to weigh a kilo, when weighed in a vacuum ; 4° C. is the temperature commonly taken as that of the greatest density of water ; 15° C. is probably the temperature most commonly used ; 15.5° C. is used as an approximate equivalent of 60° F.; 15.555+° C. is the true 60° F.; 16.666+° C. equals 62° F., commonly used in England ; 17.5° C. is the temperature proposed by Mohr originally ; 20° C. is the temperature adopted by the Physikalish-Technische Reichsanstalt for polariscopic apparatus ; and 22° C. is a temperature proposed and advocated by Oldberg before the U. S. Pharmaceutical Association but not adopted by them. Under the second type are inserted only the values for temperatures at which apparatus is actually for sale together with those for 22° C.

In discussing the merits of the different types No. II may be neglected, since it is only used to a limited extent, and the principle upon which it is based holds good only for water. The real contention is between types I and III, and it will be noted at 15° C., for instance, that the errors possible are very considerable if part of the apparatus used in an analysis is of one type and part of another. Suppose, for example, a solution is made up to one liter in a flask of the first type and then 100 cc. taken for a determination in a pipette of the third type. The result will be that an error of 1/500 of the whole amount will be introduced into the result. Other instances might be mentioned but this is certainly sufficient to show the necessity for agreement as to the type to be used. It should be stated also before leaving this point, that the German Bureau of Weights and Measures only receive, for testing, apparatus graduated for 15° C. and of type I and that the published opinions of those who have made a study of the subject are almost universally in favor of the same type.

In view of the above facts, Table II, showing the results of tests actually made upon a series of flasks representing at least five and possibly six German and American makers, is of inter-

est. In the first column the flasks are numbered for convenience in reference; in the second are shown the labels; in the third the number of the type inferred from the label; in the fourth the volume or weight actually contained, provided the inference of the type from the label is correct; in the fifth the type inferred from the actual contents found by experiment; and in the last, the volume or weight contained, provided the second inference of the type is correct, appears.

TABLE II.

TESTS OF FLASKS FROM DIFFERENT MAKERS.

No.	Label on flasks.	Type inferred from label.	Volume or weight at marked temperature if type inferred from label is correct.	Type inferred from contents.	Volume or weight at marked temperature if type inferred from contents is correct.
1	500 ccm. E+ 15° C.	I	500.002 cc.	I	500.002 cc.
2	1000 Gr. 15° C.	III	1000.453 grams	III	1000.453 g'ms
3	1000 c.c. 60° F.	I	1002.149 cc.	III	1000.112 cc.
4	1000 c.c. 60° F.	I	1002.388 cc.	III	1000.350 cc.
5	1000 ccm. 15° C.	I	1002.309 cc.	III	1000.355 cc.
6	1000 cc 60° F.	I	1001.056 cc.	II	1000.098 cc.
7	1 liter 60° F.	I	1001.120 cc.	II	1000.162 cc.
8	1000 c.c. (No. temp.)	I	998.991 cc. (at 15° C.)	Unknown	
9	1000 c.c. 60° F.	I	1002.599 cc.	III	1000.561 cc.
10	1000 cc 15° C.	I	1000.017 cc.	I	1000.017 cc.

It will be seen that the labels on flasks 1, 2, and 10 are the only ones from which the type was correctly inferred, and that flask 2 showed a variation of over ±0.3 of a gram from the supposed contents. This limit of variation, it should be mentioned, is the one adopted for liter flasks by the German Bureau of Weights and Measures, and can be easily attained in practice. Flask 8 may be called grossly inaccurate, as it is impossible to infer from the contents what type the manufacturer had in mind. No temperature for working is given upon it. The other six flasks are all wrongly or insufficiently marked for distinguishing the type to which they belong, and 4, 5, and 9 are not within the above-mentioned limits.

Aside from the type, the most important question to be settled would seem to be the temperature at which volumetric apparatus should be standard. It is assumed for the purposes of this discus-

sion that every one prefers ware graduated according to type I or, in other words, containing the named volume, as distinguished from the weight, at the specified temperature. We may then proceed to discuss the various figures given under this type in Table I.

The volumes and weights at 22° C. given in the sixth and seventh columns of this table, are supposed to be the volumes and weights contained at the most commonly occurring temperature of the average laboratory. This temperature was selected for two reasons: First, Kilgore, by "a long series of experiments," found that the average temperature of his laboratory during the working day was 21.8° C.; and secondly, it is approximately the temperature which has been found most comfortable for people not doing manual labor and located in rooms having artificial ventilation.

From the volumes given in the sixth column it will be seen that the errors incident to using apparatus, standard at the temperatures given, when it is at the ordinary temperature of a room, may amount to from 0.45 cc. per liter with that standard at 3.93° C., to nothing with that standard at 22° C., and furthermore that the error in the case of apparatus standard at 15° C., would amount to nearly two-tenths cc. per liter. It may be claimed that it is perfectly possible to use flasks at 15° C. and that in other apparatus, since it is commonly used for volumes below 100 cc., the error would not be appreciable. This view might perhaps be accepted if the temperature never went above 22° C., but many of us, particularly in commercial laboratories, have been obliged to use burettes and pipettes at temperatures as high as 30° C., with the result that this error becomes appreciable, while if the apparatus were standard at 22° C., the error in using it at 29° C. would be the same that now obtains in using apparatus standard at 15° C. when at 22° C.

Considering the different temperatures individually, it is found that 3.93° C. is the temperature at which the brass gallons furnished the different states by the U. S. Government are standard, but that neither this temperature nor 4° C. is in general use. The temperatures 15.5° C. and 60° F. are gradually going out of use in this country. 62° F. is a temperature which has little or no foothold outside of England and certainly

would be useless as a standard temperature in this country. 17.5° C., the temperature originally proposed by Mohr, appears to be gaining some favor in this country for a general temperature, although apparatus standard at that is not regularly on the market as far as the writer knows. 20° C. does not appear to be used except for polariscopic apparatus. 22° C. would seem to be the most natural temperature for use in this country if it were not for the confusion which would arise from other standards being used in other countries. But this confusion already exists and can hardly become worse by an attempt to crystallize chemical usage in this country at the most convenient temperature. It would seem that if confusion in regard to this point were such an obvious disadvantage, that a practical uniformity of usage would have already resulted by general consent. Looking at the question from a national rather than an international point of view, it is difficult to see the advantage of using any temperature below the average or the most common one of our laboratories; and surely there can be no reason, from this point of view, for discarding 15° for 17.5°, or any other temperature below 20° C. Any line of reasoning which led to the adoption of 15° C., or any other temperature above that of the greatest density of water, would seem to be still more favorable to 22° or a similar temperature.

In the writer's opinion, the most commonly occurring temperature represented by even centigrade degrees, rather than the average temperature of the laboratory, ought to be considered the best temperature for general use.

In order to secure uniformity and accuracy in using volumetric apparatus, there are three minor points which must certainly be taken into account. These are, the method of reading the meniscus, the rapidity with which delivery takes place in a burette or pipette, and the time allowed for draining in using apparatus graduated to deliver rather than to contain.

There seems to be a practical agreement in reading the extreme bottom of the meniscus, but in the times of delivery and of draining, anything but uniformity prevails. The German Bureau of Weights and Measures have a standard practice in regard to all three of these points, an account of which they have published, together with other regulations in regard to

graduated ware tested by them. A translation by Mr. E. E. Ewell, of this article, is to be found in an appendix to the "Proceedings of the Fourteenth Annual Convention of the Association of Official Agricultural Chemists." The original reference is *Zeitschrift für angewandte Chemie*, 1893, pp. 557–559.

For the sake of showing the probable errors in checking graduated glassware, Table III, giving the results of ten determinations of the contents of the same liter flask, together with the probable error in any one observation, and the probable error in the mean, is introduced.

TABLE III.

DUPLICATE TESTS OF FLASK NO. 3.

Experiment No.	Contents in cubic centimeters at the specified temperature.
2	1002.108
8	1002.110
4	1002.118
9	1002.129
5	1002.133
7	1002.163
10	1002.164
3	1002.174
6	1002.183
1	1002.206

Probable error of any one observation ±0.0228.

Mean 1002.149

Probable error of Mean ±0.0072.

The method used in these determinations, as well as in those of Table II, was to weigh the flask, fill it with boiled distilled water, and allow it to remain near the balance-case until the temperatures of the air and water were within 1° C. of each other. Then water was removed until the proper reading was obtained and the flask introduced into the balance and weighed by the method of Gauss. On removing the flask from the balance-case, the reading was checked to show that no appreciable expansion of the water had taken place, and the temperature of the water noted. The dry and wet bulb thermometers, the barometer and its thermometer, were also read. From the data thus obtained the values given in Tables II and III were calculated.

The most important source of error in this work was found to

be in taking the temperature of the water, for a variation of 0.1° C. made a difference in the final contents of the flask of approximately 0.02 cc. The thermometer used in the work was thoroughly tested and found to be correct within 0.1° C.

The variations in the buoyant effect of the air, due to variations in the barometer, were also taken into account, but it required a variation of fifteen mm. in the corrected reading to produce the same effect upon the weight of a liter of water that was produced by 0.1° in temperature. The barometer readings were not corrected for variation of the latitude from 45°, which, as the latitude was approximately 40°, would have introduced a correction of —0.35 for 760 mm. ; or for elevation above the sea-level, which as it was only about twenty-five meters, would have introduced a correction of —0.004 mm. Corrections for tension of aqueous vapor and temperature were, however, introduced, the values given in "Smithsonian Meteorological Tables" for 1896 being used.

The coefficient of cubical expansion of glass was assumed to be 0.000025. The very improbable error of two in the second significant figure of this number, would amount to only 0.014 of a gram in the final weight of a liter of water under average conditions.

The density of the weights was assumed to be eight and three-tenths, and it was found that an error here of one-tenth would result in an error of approximately 0.0017 of a gram in the final weight of the water.

The buoyant effect of the air upon the weight of the flask was assumed to be a constant.

The table giving the density of water at various temperatures was furnished by the Office of Standard Weights and Measures, at Washington, and is the one used by them. The values are those determined by M. P. Chappuis and published by the International Bureau of Weights and Measures in "Proces-Verbaux des Seances" for 1892. The table giving the weight of a liter of air at various temperatures, was furnished by the same office. It was computed by Dr. O. J. Broch, from Regnault's observations, and published in Vol. I of "Travaux et Memoires du Bureau International des Poids et Mesures." It was found that by using different data for the densities of water and the

weight of a liter of air or by using some of the published tables for obtaining the weight of a volume of water at different temperatures, an error of two-tenths of a gram might be introduced into the calculated weight of a liter.

The weights used had been compared with a standard set, originally tested and furnished with a table of corrections by the U. S. Office of Standard Weights and Measures, so that all weights were in terms of the International kilogram.

The balance was made especially for this kind of work, with large bows and pans. A variation of one division in the rest-point corresponded to six milligrams with a load of 1200 grams in each pan.

It remains for us to consider how the individual members of this society may advance the cause of uniformity in volumetric apparatus. There are two parties to be kept in mind, who look at this matter from entirely different points of view; namely, the manufacturer and the consumer. The manufacturer can be influenced only by the demands of his customers. If any considerable number of them ask for one thing, although he may decline the first few orders, the constant dropping will finally wear away the stone, and the article asked for will be added to his regular stock list.

Therefore, it must remain for us as individual customers, after committees, etc., have furnished the necessary information, to produce uniformity in the graduation and use of volumetric apparatus by instituting an overwhelming demand for the proper kind.

LABORATORY AND GRADUATING DEPARTMENT
OF WHITALL, TATUM & CO., August, 1898.

THE ALKALINE REACTION OF SOME NATURAL SILICATES.[1]

BY F. W. CLARKE.

Received August 29, 1898.

THAT pure water exerts a distinct solvent action upon many natural silicates has long been known. As far back as 1848 the Rogers brothers published a series of observations upon this subject,[2] and showed that some species of minerals would

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *Am. J. Sci.* (2), 5, 401.

give an alkaline reaction to test paper. They did not, however, give details concerning the individual minerals thus investigated. The more recent researches of Daubrée and of Cossa are well known.

By the use of phenolphthalein as an indicator the alkalinity of many silicates can be demonstrated with the utmost ease, and the experiments described below serve to bring out very clearly the relative decomposability of certain minerals and rocks by pure water. The method adopted was as follows: A series of glass-stoppered bottles was placed against a white background. In each bottle half a gram of finely pulverized mineral was put, and then fifty cc. of distilled water, containing a very little alcoholic phenolphthalein, was added. As the indicator was mixed, once for all, with the total amount of water taken for the entire series, the twenty-two samples examined were treated exactly alike. Two of the bottles were filled with the water and indicator in blank, in order that possible action upon the glass itself might be detected if it occurred. The two blanks, however, remained colorless during the two weeks through which the experiments lasted. The results obtained were as follows:

Muscovite.—A doubtful trace of coloration, which soon disappeared.

Lepidolite.—Like muscovite.

Phlogopite.—The peculiar non-fluoriferous variety from Edwards, N. Y. Gave a very distinct, permanent, pink coloration.

Orthoclase.—A trace of coloration which increased for a few days and then faded.

Oligoclase.—The transparent variety from Bakersville, N. C. Distinct and permanent, but pale coloration.

Albite.—From Amelia County, Va. Gave a good, permanent, alkaline reaction.

Leucite.—A slight reaction at first, which faded in a few days.

Nephelite.—The elaeolite from Litchfield, Maine. Good coloration, but partly fading in time.

Cancrinite.—Litchfield, Maine. Gives a deep rose coloration, which is permanent.

Sodalite.—From Canada. A deep, permanent rose color.

Spodumene.—The transparent, yellow variety from Brazil. A good reaction, but gradually fading.

Scapolite.—The wernerite from St. Lawrence County, N. Y. Gave a faint, evanescent trace of coloration.

Laumontite.—A doubtful trace of coloration.

Stilbite.—Faint, evanescent coloration.

Chabazite.—Like stilbite.

Heulandite.—Slight reaction, but distinct.

Thomsonite.—Variety lintonite. A fairly strong reaction, fading in time.

Analcite.—Good alkaline reaction.

Natrolite.—From Bohemia. Strong coloration, permanent.

Pectolite.—From Bergen Hill. Gave a very deep rose color.

Apophyllite.—From Bergen Hill. A very deep rose color.

In nearly every case the reaction was obtained at once, showing a more rapid action of water upon the silicate than had been anticipated. In some instances fading is noted. This is doubtless due, in general, to the action of light; but in certain cases the colored solution separated into two layers, the color being wholly in the lower. Here the color was really held as a coating upon the fine solid particles, and as they subsided the appearance of stratification was produced. Towards the end of the experiments the mineral aegirite was added to the series. This also gave a strong alkaline reaction and a fairly deep rose color.

A neat method of demonstrating the reactions described above is the following: Place a little of the mineral to be tested in a watch-glass upon a sheet of white paper. Add a drop of alcoholic phenolphthalein solution, and then a few drops of pure water; in most cases the reaction is given instantaneously. Orthoclase gave no coloration, leucite a trace, and scapolite a trace; albite, nephelite, and phlogopite furnished distinct reactions. Under the same circumstances thomsonite, aegirite, natrolite, cancrinite, sodalite, pectolite, and apophyllite gave immediately a deep, rich, rose color. The strongest alkaline reactions seemed to be given by pectolite and apophyllite.

In general, the order of intensity of the color produced was what might have been expected. Among the micas, muscovite and lepidolite showed little or no solubility, while phlogopite

was distinctly attacked. In nature the magnesian micas are far more easily alterable than muscovite, a fact which is reiterated by these experiments. Again, orthoclase was slightly dissolved, albite much more so, and oligoclase gave a reaction between the two; that is, more than the one, less than the other. In other words, the plagioclase feldspars alter more easily than orthoclase, as is apparent in the study of the rocks themselves.

In order to bring out the latter point more clearly, a series of rocks which had been analyzed in the laboratory of the U. S. Geological Survey, was placed in a row of bottles, and treated just as the mineral species had been, with water and phenolphthalein. A granite and an amphibole gabbro gave no alkaline reaction. A rhyolite, trachyte, leucite basalt, feldspar basalt, and diorite gave faint traces of color. Granitite, gneiss, phonolite, diabase, and camptonite yielded distinct alkaline colorations.

In all of these instances the production of color is doubtless due to the solution from the mineral or rock of alkaline silicates. The noteworthy point is the quickness with which the reaction can be obtained. With minerals like cancrinite, sodalite, natrolite, pectolite, and apophyllite, the reaction is striking enough to be used as a lecture-table experiment.

[CONTRIBUTION FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SOLUBILITY OF SALTS OF WEAK ACIDS IN STRONGER ACIDS.[1]

BY ARTHUR A. NOYES AND DAVID SCHWARTZ.

Received August 29, 1898.

1. PURPOSE OF THE INVESTIGATION.

THE theory of the influence of one electrolyte on the solubility of another whose ions differ from those of the first, has up to this time, in spite of the practical importance of the question, been developed and tested only in a very incomplete way. A few years ago, to be sure, the influence on the solubility of a strongly dissociated salt by another of approximately the same dissociation was calculated by one of us,[2] and was experimentally determined in the case of thallium chloride in

[1] Read at the Boston Meeting of the American Chemical Society, August, 1898.

[2] *Ztschr. phys. Chem.*, 6, 262.

the presence of potassium nitrate and sodium acetate, an approximate agreement being found to exist. A case of greater importance, however, is that in which a weakly dissociated substance is formed by the reaction, such as takes place in the action of a strong acid on the salt of a weaker acid; for in that case the change in solubility is very great. The purpose of this article is to derive theoretically the equations applicable to this case, and to present the results of an experimental investigation of the correctness of these equations. We have accordingly determined the solubility of silver benzoate in nitric acid, a very strong acid, and in chloracetic acid, a comparatively weak one at different concentrations, and compared the observed with the theoretical values. We will first describe the method of carrying out the experiments and then present the results.

2. DESCRIPTION OF THE EXPERIMENTS.

The silver benzoate was prepared by adding to an excess of commercial benzoic acid a solution of sodium carbonate, boiling until the solution was freed from carbon dioxide, and then treating the solution with silver nitrate. The precipitate thus obtained was washed with water and crystallized twice out of boiling water. Its purity was established by ignition and weighing the resulting silver; the amount found agreed with that calculated in two determinations within two-tenths milligram.

The nitric acid solution was prepared from a commercial chemically pure acid which was free from chlorine and which on evaporation left only an inappreciable residue. The chloracetic acid consisted of that portion of a commercial sample which boiled between 185° and 186°. The strengths of these solutions were determined with a sodium hydroxide solution which had been titrated against a sample of succinic acid, the purity of the latter having been proved by a measurement of its electrical conductivity.

The saturation of the solutions was effected by rotation in the previously described apparatus[1] at a temperature of 25°. In each case the determinations were made in pairs, so that the condition of saturation was approached from a higher as well as

[1] *Ztschr. phys. Chem.*, 9, 603.

from a lower temperature. After a rotation of at least eight hours, the solutions were filtered, since they would not completely settle; and a portion of 100 cc. was at once measured out with a pipette and titrated with a twentieth-normal solution of potassium thiocyanate with the addition of nitric acid and ferric alum as indicator.

3. THE EXPERIMENTAL RESULTS.

The following tables contain the results of all the solubility determinations. The numbers express the millimols of silver benzoate dissolved in one liter. The values which were obtained by cooling the solutions to 25° are placed under the heading "supersaturated," while those obtained by heating to 25° are designated as "undersaturated."

SOLUBILITY OF SILVER BENZOATE IN PURE WATER.

Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
11.40	12.04	11.61[1]	11.68
11.43	12.44	11.61[1]	11.62
11.43	12.74	11.63[1]	11.66
11.49	12.27	11.46	11.97
11.47	12.14	12.14[2]	12.35
11.42	12.24	11.45	13.86[3]
11.42	11.96	11.40	12.86
....	....	11.43	12.92

Mean of the undersaturated solutions: 11.47 ± 0.017 or 11.44 ± 0.007.

Mean of the supersaturated solutions: 12.21 ± 0.091.

SOLUBILITY OF SILVER BENZOATE IN NITRIC ACID.

Concentration of acid. 4.435 millimols per liter.		Concentration of acid. 8.870 millimols per liter.		Concentration of acid. 8.915 millimols per liter.	
Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
13.97	14.75	17.00	17.34	17.15	17.57
13.92	15.07	16.96	18.20	17.15	18.07
13.95	14.87	17.19	17.11	....	....
13.94	14.86	16.75	17.64	....	....
14.21[1]	14.16[1]	....	....	....	....
13.95	14.62	....	....	....	....
13.95	14.83	16.98	17.57	17.15	17.82
±0.006	±0.054	±0.060	±0.174	±0.000	±0.179

[1] Omitted in the calculation of the second mean.
[2] Omitted in the calculation of both means.
[3] Omitted in the calculation of the mean.

Concentration of acid. 17.74 millimols per liter.		Concentration of acid. 17.83 millimols per liter.		Concentration of acid. 26.74 millimols per liter.	
Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.
23.27	24.07	23.47	24.83	30.70	31.10
23.23	24.21	23.55	24.97	30.68	35.12
23.46[1]	23.93	....	....	30.77	31.93
23.21	23.97	....	....	30.67	33.30
23.24	24.05	23.51	24.90	30.71	32.86
±0.013	±0.048	±0.029	±0.050	±0.016	±0.674

SOLUBILITY OF SILVER BENZOATE IN CHLORACETIC ACID.

Concentration of acid. 3.935 millimols per liter.		Concentration of acid. 7.87 millimols per liter.		Concentration of acid. 15.74 millimols per liter.	
Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.	Under-saturated.	Super-saturated.
13.86	13.86	16.10	16.18	20.92	21.13
13.81	14.29	16.10	16.36	20.94	25.09[1]
13.86	14.16	16.12	16.56	20.90	21.40
13.86	14.16	16.14	16.38	20.95	21.09
13.85	14.12	16.12	16.37	20.93	21.21
±0.019	±0.064	±0.008	±0.050	±0.010	±0.076

The relatively large number of solubility determinations in pure water were carried out because the supersaturated and the undersaturated solutions did not correspond. The seven pairs of values in the first two columns were obtained after six hours' rotation of the solutions; the first five in the third and fourth columns, after twenty-four hours; and the last three in these columns, after seventy-two hours. The saturation seems, however, to depend much more on the quantity and physical condition of the solid substance than on the time. As is seen, the mean of the supersaturated solutions is six and four-tenths per cent. higher than that of the undersaturated. From the fact, however, that the separate undersaturated values agree well with one another, while the supersaturated ones show large variations, the former may be considered as essentially correct. In the two cases, the average deviations of the means amount to 0.15 and 0.75 per cent. respectively, and if these values were combined according to the laws of probability, then a relative weight of only four per cent. would have to be ascribed to the supersaturated. Paul[2] had exactly the same experience in his researches on the solubility of certain organic acids whose phys-

[1] Omitted in the calculation of the mean.

[2] *Ztschr. phys. Chem.*, 14, 112.

ical condition is similar to that of silver benzoate. He also came to the conclusion that the undersaturated values are the reliable ones. The same difference between the results of the two methods of determination also exists in the presence of the two acids. We have therefore taken the mean value of the undersaturated solutions as the more reliable. These will be brought together in a table below.

4. THE THEORY OF SOLUBILITY EFFECT.

We will now determine whether the experimental values are in accordance with the requirements of the theory of solubility effect. In order to do this, it is necessary to derive from the laws of mass-action the equations which should express the relation between the solubility of the silver benzoate in pure water and its solubility in the solutions of nitric acid and of chloracetic acid. This we will now proceed to do in a general form.

The problem is the determination of the solubility of a di-ionic electrolyte AB in a solution which contains a known amount of a second di-ionic electrolyte CD. (An influence on the solubility takes place, since by metathesis certain amounts of the substances AD and CB are produced.) The solubility of the body AB in pure water and the dissociation relations of all the substances involved are to be assumed to be known.

First it is to be noticed that the following eight substances are present in the solution: the four undissociated substances AB, CD, AD, and CB; and the four ions, A, B, C, and D. We will designate the concentrations of the ions by these same large letters, and those of the undissociated molecules AB, CD, AD, and CB by the small letters a, b, c, and d respectively. If now the solution contains the known amount n of the substance CD in one liter, and the solubility in it of the substance AB is m, evidently the following equations hold true:

$$a + c + A = m, \quad (1)$$
$$a + d + B = m, \quad (2)$$
$$b + c + D = n, \quad (3)$$
$$b + d + C = n. \quad (4)$$

Further if m_0 is the solubility of AB in pure water, and a_0 is

the corresponding dissociation, we obtain as the expression of the solubility principles: [1]

$$a = m_0(1 - a_0). \tag{5}$$

$$A \times B = m^2{}_0 a^2{}_0 = k_a, \tag{6}$$

where k_a is used for brevity to express the product $m_0{}^2 a_0{}^2$. Finally the following three dissociation equations apply:

$$\frac{C \times D}{b} = k_b, \tag{7}$$

$$\frac{A \times D}{c} = k_c, \tag{8}$$

and

$$\frac{C \times B}{d} = k_d, \tag{9}$$

where k_b, k_c, and k_d are the dissociation constants of the substances CD, AD, and CB respectively.

We now have nine equations and nine unknown quantities; namely, the concentrations of the eight different kinds of molecules and the value m. Theoretically then this latter quantity can be determined and we have convinced ourselves that the necessary eliminations can be carried out; that is to say, an equation can be obtained which contains as an unknown quantity only the quantity m, but the equation is of a high degree in m and consists of a very large number (probably a hundred or more) of terms. Accordingly the calculation has not been carried out, especially since this most general case finds no practical application, because at least one of the substances CD, AD, and CB must be a salt to which the theoretical laws of dissociation do not apply.

There is a possibility of simplifying the problem since a sufficiently accurate knowledge of one or two of the three values b, c, and d can be obtained from other sources, whereby the corresponding dissociation equations can be dispensed with in the elimination, and the algebraic solution becomes much simpler. For, the dissociation of a substance in pure water can always be determined by means of conductivity measurements, and in the case of a largely dissociated substance, like a salt, or a strong acid or base in dilute solution, its disso-

[1] *Ztschr. phys. Chem.*, 4, 372; 9, 603.

ciation is influenced so little by the presence of other substances that its undissociated amount can be quite accurately estimated by a short approximation process. Since now at least one of the three bodies CD, AD, and CB must be a salt, it is always possible to simplify in this manner.

The simplest cases are those in which all three of the substances CD, AD, and CB, or the last two of these, are strongly dissociated substances, so that the quantities b, c, and d, or the last two of them, can be determined from the conductivities of the salts in pure water. The solubility of thallium chloride in potassium nitrate, referred to at the beginning of this article, is one example of this kind. That of silver benzoate in sodium nitrate would be another. This case, is not, however, of present interest, as we have no new experiments of the kind to communicate.[1]

The next simplest case is that where CD and AD (or CB) are strongly dissociating substances, while CB (or AD) is only slightly or moderately dissociated. In this case the quantities b and c (or d) can be determined from conductivity measurements, and can therefore be regarded as known quantities in the derivation of the final equation, so that equations (7) and (8) (or (9)), which contain them, can be dispensed with. The solubility of the silver benzoate in nitric acid is a case of this kind; for nitric acid and silver nitrate are strongly dissociated, and benzoic acid is weakly dissociated.

In order, now, to derive this equation, we assume b and c to be known, so as to have a definite case under consideration, and proceed as follows: For brevity we put

$$m - a = x, \tag{10}$$

and

$$n - b = l, \tag{11}$$

l being a known quantity, and x the quantity to be determined. By elimination between equations (1), (2), and (6), we obtain:

$$d = \frac{x^2 - cx - k_a}{x - c}.$$

Furthermore we obtain by combining equations (2), (4) and (9): $d = \frac{1}{2}(x + l + k_d \pm \sqrt{x^2 + l^2 + k_d^2 + 2xk_d + 2lk_d - 2lx})$.

[1] For a full discussion of the theory in this case see Noyes: *Ztschr. phys. Chem.*, 27.

If now we place these two values of d equal to each other and simplify, we obtain the following expression:

$$x^3 + (r - 2c)\,x^2 + (c^2 - rc - rn + rb - k_a)\,x + (rcn - rcb + k_a c - k_a r) = 0, \qquad (12)$$

in which $r = \frac{k_a}{k_d}$. By means of this equation we can calculate the value of x, since all the other values are known, and from this we obtain the solubility m by equation (10). In the case where the substance AB is difficultly soluble and the value n is not very great, the quantities b and c are negligible. Then the following equation applies:

$$x^3 + rx^2 - (rn + k_a)x - k_a r = 0. \qquad (13)$$

If further x is very small relatively to r, the cubic term may be neglected. In this case:

$$x^2 - (n + k_d)x - k_a = 0. \qquad (14)$$

The remaining case to be considered is that where only the substance AD (or CB) is strongly dissociated, both CD and CB (or AD) being only slightly or moderately dissociated, so that they follow the theoretical dissociation-law. In this case only the quantity c (or d) can be regarded as known, and only equation (8) (or (9)) can be dispensed with in the derivation of the solubility equation. For the sake of definiteness we assume c to be known.

The solubility of silver benzoate in chloracetic acid is an example of this case, for chloracetic acid and the benzoic acid produced by the metathesis are weakly dissociated, and the silver chloracetate is much dissociated.

To derive the solubility equation, equations (3), (4), and (7) are solved for b with elimination of C and D, whereby we obtain:

$$2b = -(c + d - 2n - k_b) \pm \sqrt{(c + d - 2n - k_b)^2 + 4(cn + dn - n^2 - cd)}.$$

Eliminating B and C from equations (2), (4), and (9), we obtain:

$$2b = \frac{2(n - d)(x - d) - 2k_d d}{(x - d)}.$$

If now we place these values of $2b$ equal to each other, simplify, and substitute in the resulting equation the value of d derived from equations (1), (2), and (6), *viz.*, $d = \frac{x^2 - cx - k_a}{x - c}$, after simplification we obtain:

$$rx^5 + (1 - 3cr)x^4 + (3c^2r - 3c + k_b - 2k_d)x^3 + (4ck_d - c^3r + 3c^2 - 2k_a - 2ck_b + s)x^2 + (k_ak_d - 2c^2k_d + 3ck_a - c^3 - k_ak_b + c^2k_b - ns - cs)x + (k_a^2 - ck_ak_d - c^2k_a + ck_ak_b + cns - k_as) = 0, \quad (15)$$

in which $x = m - a$; $r = \frac{k_d}{k_a}$; and $s = \frac{k_ak_b}{k_d}$. In very dilute solutions, or in general as an approximation, c may be placed equal to 0, when follows:

$$rx^5 + x^4 + (k_b - 2k_d)x^3 + (s - 2k_a)x^2 + (k_ak_d - k_ak_b - ns)x + (k_a^2 - k_as) = 0. \quad (16)$$

In certain cases, for example, when k_b is negligible in comparison with k_d, or the reverse, a further simplification may easily be made.

COMPARISON OF THE EXPERIMENTAL AND THEORETICAL VALUES.

We have, now, by means of equation (12), calculated the theoretical solubility of silver benzoate in the various solutions of nitric acid, making use of the following data: $k_a = m_0^2a_0^2 = 0.0000932$ (since the solubility in pure water, $m_0 = 0.01144$, and the corresponding dissociation-value, $a_0 = 0.844$, according to conductivity measurements of our own); the dissociation constant of benzoic acid, $k_d = 0.000060$, according to Ostwald's measurements, whence the ratio $r = 1.553$. The values of c in the different cases were deduced from the conductivity of silver nitrate as determined by Kohlrausch. The equations were solved in this case and also in that of the chloracetic acid, by repeated substitution of estimated values of x until the exact root was found.[1]

The solubility of silver benzoate in chloracetic acid has been calculated by equation (15), using the same values of k_a and k_d, as before, putting the dissociation constant of chloracetic acid,

[1] For further details of the method of calculation, reference is made to a more extended article on the theory in the current volume of the *Zeitschrift für physikalische Chemie*.

$k^5 = 0.00155$, in accordance with the measurements of Ostwald, and determining c from conductivity measurements.

In the following tables are given the experimental and the theoretical values, together with the percentage differences between them.

SOLUBILITY OF THE SILVER BENZOATE IN NITRIC ACID.

Experiment No.	Concentration of the nitric acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	.....	.....
II	0.004435	0.01395	0.01406	+0.78
III	0.008870	0.01698	0.01703	+0.29
IV	0.008915	0.01715	0.01706	−0.53
V	0.01774	0.02324	0.02390	+2.76
VI	0.01783	0.02351	0.02396	+1.89
VII	0.02674	0.03071	0.03159	+2.79

SOLUBILITY OF THE SILVER BENZOATE IN CHLORACETIC ACID.

Experiment No.	Concentration of the chloracetic acid.	Found solubility.	Calculated solubility.	Percentage difference.
I	0.00	0.01144	.....	.....
II	0.003935	0.01385	0.01368	−1.24
III	0.00785	0.01612	0.01588	−1.51
IV	0.01574	0.02093	0.02117	+1.13

The agreement between the found and the calculated values is very satisfactory, especially considering the large number of dissociation values used in the calculation; consequently the solubility principles and the validity of the theoretical laws of dissociation in the case of weakly dissociated acids are again confirmed. It is specifically shown by this investigation that the solubility of silver benzoate is increased both by nitric acid and chloracetic acid in such a way that the product of the concentrations of the Ag and the $C_6H_5CO_2$ ions remains constant.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SOLUBILITY OF ACIDS IN SOLUTIONS OF THE SALTS OF OTHER ACIDS.[1]

BY ARTHUR A. NOYES AND EDWARD S. CHAPIN.

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I. PURPOSE OF THE INVESTIGATION.

IN an article published elsewhere by one of us,[2] the theory of the influence of one di-ionic electrolyte on the solubility of

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *Ztschr. phys. Chem.*, 27.

another with different ions, was developed for the different cases actually occurring. Certain experiments made with the object of testing the theoretical equations so derived have been presented in the preceding paper; but there remains an especially important case to which the application of the theory has not yet been experimentally tested,—that involving the effect of a neutral salt of a partially dissociated acid on the solubility of another acid, likewise only partially dissociated. An example of this kind would be the effect of sodium acetate or of sodium formate on the solubility of benzoic acid, and we have in fact investigated this case, using each of the salts at different concentrations.

2. DESCRIPTION OF THE EXPERIMENTS.

In the first place the preparation of the substances and of the solutions employed will be described. The benzoic acid was prepared from a commercial sample by dissolving in the sodium carbonate solution, *partially* precipitating with dilute hydrochloric acid, and twice recrystallizing from boiling-water. As powdered benzoic acid probably saturates a solution much more quickly than does the crystallized form, the acid was then melted and finely pulverized. It was shown by qualitative test to be free from chlorine.

The sodium acetate and sodium formate used were prepared by twice recrystallizing the commercial salts. Solutions of these were made up by weighing out roughly the air-dried salts; and their concentrations were then accurately determined by evaporating measured portions with hydrochloric acid in platinum dishes, moistening the residue with the acid, and igniting gently until a constant weight was obtained. The three check determinations made in each case agreed within three-tenths per cent.

The solubility determinations were made by rotating for about sixteen hours at 25° in the previously described apparatus[1] bottles containing pure water or the solutions of sodium acetate or sodium formate and an excess of the solid benzoic acid. In one-half of the experiments the state of saturation was approached by cooling the solutions from a higher temperature,

[1] *Ztschr. phys. Chem.*, 9, 606.

and in the other half by warming from a lower temperature. Portions of the solution were quickly filtered, and twenty-five cc. measured out with a pipette and titrated, using phenolphthalein as an indicator, with a barium hydroxide solution which had been standardized by means of calcium carbonate and succinic acid, and which was 0.02936 normal.

3. THE EXPERIMENTAL RESULTS.

The following tables contain the results of all the solubility experiments. The numbers express the quantity of dissolved benzoic acid in millimols per liter. Those values which were obtained by cooling the solutions down to 25° are placed under the heading "supersaturated;" while those obtained by heating up to 25° are designated as "undersaturated."

SOLUBILITY OF BENZOIC ACID IN PURE WATER.

No.	Supersaturated.	Undersaturated.
1	27.92	28.02
2	27.80	27.79
3	28.10	27.88
4	28.22	27.80
5	27.96	27.81
Mean	28.00	27.86
	±0.058	±0.032

SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTIONS.

	Concentration of the salt. 13.21 millimols.		Concentration of the salt. 26.41 millimols.		Concentration of the salt. 52.82 millimols.	
Experiment number.	Supersaturated.	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.	Undersaturated.
1	38.84	38.71	48.55	48.32	64.92	64.58
2	....	....	48.44	48.28	64.90	64.70
Mean..	38.84	38.71	48.50	48.30	64.91	64.64

SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTIONS.

	Concentration of the salt. 14.14 millimols.		Concentration of the salt. 28.28 millimols.		Concentration of the salt. 56.57 millimols.	
Experiment number.	Supersaturated.	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.	Undersaturated.
1	34.65	34.65	38.85	38.83	45.36	45.24
2	34.52	34.42	39.00	38.84	45.33	45.27
Mean..	34.59	34.54	38.93	38.84	45.35	45.26

It will be seen from an examination of the tables that the supersaturated values are, in general, from three-tenths to five-tenths per cent. higher than the undersaturated values, a result which may be regarded as very satisfactory, in view of the diffi-

culty in this respect often experienced in solubility experiments with organic substances.[1] In the subsequent calculations and summary of results, the averages of the supersaturated and undersaturated mean values are adopted as most probably correct.

4. COMPARISON OF THE EXPERIMENTAL WITH THE CALCULATED VALUES.

It remains now to determine to what extent the values found as above described agree with the requirements of the theory of solubility effect. In order to determine this, we have calculated the solubility of the benzoic acid in the various salt solutions from its solubility in pure water and the dissociation relations of the substances involved, using the equation applicable to this case, derived in the preceding article of Noyes and Schwartz. This equation is

$$x^3 + (r-2c)x^2 + (c^2 - rc - rn + rb - k_a)x + (rcn - rcb + k_a c - k_a r) = 0,$$

in which

$$x = m - m_0(1 - a_0) \text{ and } k_a = m_0^2 a_0^2,$$

where m_0 and m are the solubilities of the benzoic acid in pure water and in the salt solution of the concentration n, and where a_0 is the dissociation corresponding to the concentration m_0; in which, further, $r = \frac{k_a}{k_d}$, where k_d is the dissociation-constant of the acetic or formic acid; and in which b and c represent the undissociated portions of sodium acetate or formate and of sodium benzoate respectively.

The data in the calculations by this formula are the following: The solubility in pure water m_0 was found by our experiments to be 0.02793; the dissociation a_0 corresponding to this was calculated from the dissociation constant $0.0_4 60$, determined by Ostwald, and found to be 0.0453, from which it follows that $k_a = 0.0_5 1601$. The dissociation constants k_d of acetic and formic acids are respectively $0.0_5 18$ and $0.0_3 214$. The values of b and c varied in the different cases and were determined as described in the article just referred to from the electrical con-

[1] Compare Paul: *Ztschr. phys. Chem.*, 14, 112, and the preceding article.

ductivity of the salts and measured by Ostwald ; they were in the case of the sodium acetate as follows : For

(1) $n = 0.01321$ $b = 0.00028$ $c = 0.001737$
(2) $n = 0.02641$ $b = 0.00138$ $c = 0.00448$
(3) $n = 0.05282$ $b = 0.00508$ $c = 0.001142$

and in the case of the sodium formate, for

(4) $n = 0.01414$ $b = 0.00081$ $c = 0.00133$
(5) $n = 0.02828$ $b = 0.00278$ $c = 0.00309$
(6) $n = 0.05657$ $b = 0.00886$ $c = 0.00714$

By substituting these values and the values of the constants just preceding in the algebraic equation given above, the following six numerical equations were obtained :

(1) $x^3 + 0.08547\ x^2 - 0.001303\ x + 0.0_41859 = 0$
(2) $x^3 + 0.0800\ x^2 - 0.002606\ x + 0.0_4985 = 0$
(3) $x^3 + 0.0661\ x^2 - 0.005134\ x + 0.0_44835 = 0$
(4) $x^3 + 0.004830\ x^2 - 0.0001095\ x + 0.0_41224 = 0$
(5) $x^3 + 0.001296\ x^2 - 0.0002059\ x + 0.0_45787 = 0$
(6) $x^3 - 0.006802\ x^2 - 0.0003625\ x + 0.0_42549 = 0$

Estimated values of x were substituted in these equations till the roots were found ; and from the latter the solubility was calculated by the equation : $m = x + m_0(1 - a_0)$. The solubility values so calculated are placed in the following table by the side of the mean values experimentally determined. In the last column the percentage differences between the two series of values are given.

SOLUBILITY OF BENZOIC ACID IN SODIUM ACETATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1	0.00000	0.02793	0.02793	.....
2	0.01321	0.03846	0.03878	+0.82
3	0.02641	0.04783	0.04840	+1.19
4	0.05282	0.06380	0.06480	+1.52

SOLUBILITY OF BENZOIC ACID IN SODIUM FORMATE SOLUTION.

Number.	Concentration of the salt.	Calculated solubility.	Found solubility.	Percentage difference.
1	0.00000	0.02793	0.02793	.....
2	0.01444	0.03423	0.03456	+0.96
3	0.02828	0.03858	0.03888	+0.77
4	0.05657	0.04553	0.04530	—0.50

The tables show that the agreement between the found and the calculated solubility is satisfactory. The correctness of the principles of solubility-effect and of the laws of dissociation involved in the equation used for the calculation is therefore demonstrated.

As the equation given above is quite complicated, and as the determination of the values of b and c involved is a laborious operation, it is important to show that approximately accurate results can be obtained when these quantities are neglected. In this case equation (1) becomes simplified to the following equation:

$$x^3 + rx^2 - (rn + k_a)\,x - k_a r = 0. \qquad (2)$$

The values of the solubilities calculated by the equation are given in the following table, together with those calculated by equation (1), and with the percentage differences between the two values. The first three columns of figures show the solubility in the three sodium acetate solutions, the last three that in the sodium formate solutions.

CALCULATED SOLUBILITIES.

By equation (1).....	0.03846	0.04783	0.06380	0.03423	0.03858	0.04553
By equation (2).....	0.03844	0.04798	0.06392	0.03384	0.03801	0.04391
Percentage difference	0.05	0.30	0.20	1.14	1.48	3.60

It will be seen that in the case of the sodium acetate solutions the solubility values calculated by the simpler formula are almost identical with those obtained by means of the exact formula. In the case of the formate the differences are greater, but only for the greatest concentration is it at all considerable (three and six-tenths per cent.). Therefore for acids not more soluble than benzoic acid, when dissolved in salt solutions of corresponding concentrations, the simpler equation would be sufficiently exact for most purposes.

THE COLOR OF SULPHUR VAPOR.[1]

By Jas. Lewis Howe and S. G. Hamner.

Received August 29, 1898.

OUR attention was some time since called to a curious difference of opinion on the part of chemical authorities as to the color of sulphur vapor. In twenty-nine standard text-books and reference books examined which mention the color of the vapor, thirteen different colors are given, as follows:

	Authorities.
Deep yellow	4
Orange	5
Orange to dark yellow	1
Orange-yellow	2
Brownish yellow	6
Yellowish brown	1
Amber	2
Yellowish red	1
Red	1
Deep red	2
Deep red to brown	1
Brownish red	2
Reddish brown	1

In no work was any mention found of a change in the color of the vapor with changing temperature.

In order to examine the true color of the vapor a number of experiments were carried out, which, while not complete or entirely satisfactory, nevertheless throw some light upon the discrepancies cited. The first apparatus used consisted merely of a small test-tube of hard glass, within a larger tube, also of hard glass, the smaller tube being held free from contact with the larger by means of a wire frame. The ends of both tubes were stopped with asbestos wads to prevent free circulation of the air. A piece of roll sulphur was placed in the inner tube and heated by Bunsen burners. The pure sulphur vapor could be seen in the inner tube, the hot air in the outer tube preventing the condensation of the vapor on the sides. This simple apparatus gives a good view of sulphur vapor up to the softening point of the glass. The second form of apparatus used was

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

a porcelain tube two cm. in diameter and sixteen cm. long, with the ends covered by thin sheets of mica, and the whole tightly packed in a larger iron tube by clay. The inner tube was thus not sealed perfectly, but permitted the escape of the excess of sulphur vapor on heating, though under some considerable pressure. The apparatus was heated in a muffle whose rear end was replaced by a sheet of mica. It was thus possible to have a clear view through the tube while it was heating. The temperature was gauged approximately by tubes of silver chloride (melting-point 457°), lead chloride (melting-point 498°), and potassium iodide (melting-point 634°).

In every case the sulphur, when just beginning to boil, gave a vapor which would perhaps be denominated orange-yellow. This color is almost exactly matched by a normal solution of potassium bichromate. As the temperature increases the color very rapidly deepens and loses every vestige of the yellowish tint. This corresponds to a temperature not much above 457°. On raising further the temperature, the color deepens further. The deepest color was found by several experiments to be at the temperature of about 500° (lead chloride just fused). The paler red color is matched by a solution consisting of

	Parts.
Ferric chloride (normal solution).....	1
Potassium thiocyanate (normal solution)..	2
Water	312

The deepest red is matched by a solution:

	Parts.
Ferric chloride (normal solution).....	1
Potassium thiocyanate (normal solution)..	2
Water.....	250

This is as far as the changes can be observed in the test-tubes. Heated in the muffle, immediately above 500°, the vapor begins to grow perceptibly lighter, at 634° being almost straw-color. Up to this temperature the escaping jet of sulphur vapor indicated that the tube must be filled with sulphur vapor. When this jet ceased the results became too doubtful to record. That the rapidly decreasing intensity of color was not due merely to decreasing pressure is evidenced by the fact that the color of the vapor at its darkest point was almost exactly the same in the

porcelain tube and in the test-tube, in the latter case the vapor being practically at atmospheric pressure.

The cause of the different colors applied to sulphur vapor is doubtless due to three causes:

1. The general difficulty of describing the colors of vapors, the relative intensity of which is so much less than that of our ordinary standards.

2. The fact that the color of sulphur vapor varies with the temperature.

3. Sulphur vapor condenses so readily that when boiled in a test-tube the sides of the tube are covered with a layer of the brownish red liquid, which has doubtless sometimes been mistaken for the vapor. Similarly, when sulphur fumes escape from a hot covered crucible into which sulphur has been thrown, it is the condensing sulphur mist, very deep red in color, which one sees, and not the true vapor of sulphur.

The conclusions of this paper are that the color of sulphur vapor varies with the temperature, being of an orange tint just above its boiling-point, deepening to a red which is strongest at 500°, and then becoming rapidly lighter with increasing temperature. The color at the boiling-point is that of a normal solution of potassium bichromate; that of the deepest red is that of a rather dilute solution of ferric thiocyanate.

It is hoped it may be possible to carry these experiments further, but no reservations are made of the subject if others are interested.

WASHINGTON AND LEE UNIV.,
July 1, 1898.

THE FORMATION OF ALUMS BY ELECTROLYSIS.[1]

BY JAS. LEWIS HOWE AND E. A. O'NEAL.

Received August 29, 1898.

THE work herein described had for its special end the formation of alums of manganese, and while, in this particular, success was not attained, it is felt that it is well to place the work on record, especially as phases of it are capable of further development, from which interesting results may be hoped.

Manganese salts in which the metal is trivalent, are not very satisfactorily known. Potassium and ammonium manganic

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

alums have been described by Mitscherlich, but to manganic sulphate, $Mn_2(SO_4)_3$, Franke, who has most thoroughly studied it, gives the formula $^{II}Mn\begin{matrix}SO_4\\SO_4\end{matrix}{>}{<}{}^{IV}MnSO_4$.[1] A salt of this constitution could hardly give an alum, and the literature of the manganese alums is very unsatisfactory. It was hoped by using the oxidizing action of the electric current on a solution of manganous sulphate in the presence of an alkaline sulphate, manganic alum might crystallize out, and the reaction was studied with other metals for the sake of familiarity with the method and for comparison. Incidentally several alums were obtained and analyzed which have not been previously described.

a. Iron Alums.—Apparatus: Positive electrode, a platinum dish of about 250 cc. capacity resting on a coil of heavy copper wire; negative electrode, a coil of heavy platinum wire; diaphragm, the lower portion of the porous cup of a Bunsen cell. In different experiments different batteries were used, but Bunsen or crowfoot cells were generally used.

The following is a specimen experiment: Inner solution, ferrous sulphate strongly acidified with sulphuric acid; outer solution, saturated with ferrous sulphate and ammonium sulphate, and also strongly acidified with sulphuric acid; six crowfoot cells; current, 0.04 ampère. In forty-eight hours a large crop of beautiful iron-ammonium alum crystals, of perfect octahedral form, were produced. In one experiment with solutions as above and apparatus also, except that Bunsen cells were used, with current 0.02 ampères, forty-one grams of iron ammonium alum were obtained in twenty-four hours. This method is probably applicable to the formation of this alum on a commercial scale, having as its advantages the ease with which it is conducted and the fine quality of the product. Owing to the lesser solubility of potassium sulphate, the method, while successful, does not give such good results in the formation of iron potassium alum.

The formation of iron sodium alum was tried, using solutions as above, with sodium sulphate substituted for ammonium sulphate. Current, four Bunsen cells. After twelve hours the

[1] *J. prakt. Chem.* [2], 36, 451.

outer solution (+) was pink and in twenty-four hours had become dark purple, resembling almost a solution of potassium permanganate, while oxygen bubbles were given off at the positive pole. A little ferrous sulphate solution was added, at which the color at once disappeared, but after several hours with the current, it again became dark purple. The color disappeared at once with reducing agents. The color was that of ferrates, but the presence of ferric acid is hardly probable, and the solution being strongly acid, ferrates could not be present. It seems more probable that the compound was one of persulphuric acid. No crystals could be obtained even by using a freezing mixture. Some of the solution set aside for several weeks left, on evaporation, a hard, dirty, violet crystalline mass, containing crystals somewhat triangular in form, which were very insoluble in both water and hydrochloric acid. This substance was not pure and was not further investigated.

Iron Rubidium Alum and Iron Cesium Alum, $RbFe(SO_4)_2.12H_2O$ *and* $CsFe(SO_4)_2.12H_2O$.—As no description of these alums was found in chemical literature, they were both formed and analyzed. In working with rubidium and cesium salts, a smaller form of apparatus was used, the positive pole being a platinum crucible of eleven cc. capacity, the negative pole a coil of heavy platinum wire, and the diaphragm an unglazed porcelain annealing cup. The cup was filled as above with a solution of ferrous sulphate and the platinum crucible, which rested in a ring of heavy copper wire, with a solution of ferrous sulphate and rubidium sulphate or cesium sulphate. Both solutions were strongly acid with sulphuric acid. Very considerable crops of both the rubidium and cesium alums were obtained in the form of small octahedra. They are of a delicate violet color, turning slightly greenish on exposure to the air. They resemble potassium alum in every respect except that the rubidium alum is very slightly soluble and the cesium alum almost insoluble in water.

Analysis :

	Calculated for $RbFe(SO_4)_2.12H_2O$.	Found. I.	Found. II.
H_2O	39.3	39.1	38.9
SO_4	34.9	35.2	...
Fe	10.2	11.0	..

	Calculated for $CsFe(SO_4)_2.12H_2O$.	Found. I.	II.
H_2O	36.2	36.1	36.3
SO_4	32.2	33.3	...
Fe	9.4	10.4	...

b. Cobalt Alums.—The cobalt, potassium, and ammonium alums were discovered by Marshall, whose work was the incentive to that described in this paper. The rubidium and cesium alums were made by us and have not been hitherto described. The apparatus used was the smaller form, as for the iron rubidium alum, and the experiments conducted similarly. The outer (positive) solution was kept quite strongly acid with concentrated sulphuric acid. Four Bunsen cells were used; current 0.16 to 0.19 ampère. At first it was found that in some experiments beautiful crystals were obtained in considerable quantity, in others no crystals at all. This was soon found to be due to the temperature. On nights when the laboratory was cool the crystals formed readily. By keeping the crucible with its support immersed in a beaker of water, ill effects from heating by the current were avoided and the alums readily obtained.

It is thus seen that the rubidium and cesium alums are much more readily formed than the potassium and ammonium, as would be expected. These alums are minute, deep blue octahedra, stable in dry air, but gradually decomposing in moist air with formation of cobalt sulphate; the cesium alum showed occasional cube faces. In water the alums are quickly decomposed with evolution of oxygen and reduction to cobalt sulphate. In dilute hydrochloric acid and in dilute sulphuric acid the crystals dissolve to a blue solution. In concentrated hydrochloric acid and concentrated sulphuric acid they are decomposed, giving in the latter case a brown solution.

Several methods of analysis were tried. On heating to 200° the salt becomes whitish pink, and apparently contains free sulphuric acid from its decomposition into cobalt sulphate, more or less water being thus retained. The best method of analysis was found to be the following: The salt is mixed with anhydrous sodium carbonate in a platinum boat, and heated in a combustion tube in an oxygen stream. The water is absorbed in a calcium chloride tube. The residue is treated with hot

[1] *Proc. Roy. Soc.*, Edin., 14, 203; *J. Chem. Soc.*, 59, 760.

water. The filtrate contains the Cs (or Rb) and the SO_4, which are estimated as cesium chloroplatinate and barium sulphate. The insoluble residue, cobalt oxide, is heated in a hydrogen stream and weighed as metallic cobalt.

	Calculated for $RbCo(SO_4)_2.12H_2O$.	Found. I.	Found. II.
Rb	15.5	15.9	...
Co	10.7	11.9[1]	...
SO_4	34.8	35.4	...
H_2O	39.1	37.9	38.22

	Calculated for $CsCo(SO_4)_2.12H_2O$.	Found.[3]
Cs	22.1	22.5
Co	9.8	10.2
SO_4	32.0	32.2
H_2O	36.0	36.7

c. Chromium Alums.—An experiment was tried using a solution of potassium chromate strongly acidified with sulphuric acid as electrolyte for the negative pole, and dilute sulphuric acid for the positive. After thirty-six hours no chrome alum was obtained, but considerable potassium sulphate was deposited, strongly colored green by the chromic solution present. On substituting ammonium chromate for the potassium chromate a considerable crop of chromium ammonium alum crystals was obtained at the negative pole. These crystals were very small. Four Bunsen cells were used in these experiments. This method of electrical reduction has been used by Piccini for the formation of vanadium[4] and titanium[5] alums.

d. Experiments with Manganese.—These experiments were carried out in both the large and small apparatus; with manganese sulphate and ammonium, rubidium, and cesium sulphates; with varying quantities of free sulphuric acid in the electrolytes; with different strengths of current; and at various temperatures. The solution at the positive pole in every case became deep wine color, and the higher oxide of manganese was deposited. In one case only were a few minute octahedral crystals found in a rubidium manganese solution. These were deep wine color and qualitatively contained manganese. It is not, however,

[1] As $CoSO_4$ after removal of Rb as Rb_2PtCl_6.

[2] By loss at 200°.

[3] By method described above.

[4] *Gazz. chim. ital.* **25**, [2]. 451.

[5] *Ibid.*, **25**, [2], 542.

improbable that these were crystals of common alum colored by manganese. In an experiment with ruthenium such crystals were obtained, the aluminum being probably derived from the porcelain diaphragm. In a number of cases the black precipitate at the positive pole, supposed to be manganese dioxide, when allowed to stand with concentrated sulphuric acid, showed itself under the microscope to be made up of flat, transparent, pale, wine-colored crystals, resembling elongated hexagonal plates. These are not readily soluble in water or acids. They were not further investigated.

The electrolytical method does not seem to be applicable to the formation of manganese alums from manganous salts.[1] It is hoped later to try the electrolytic reduction of manganates and permanganates.

e. Experiments with Ruthenium.—No crystallized oxy-salts of ruthenium are known. As the double salts of the trichloride crystallize well, an effort was made to obtain an alum by the electrolytic reduction of the nitrosochloride. The small apparatus was used. The solution at the negative pole was a solution of cesium ruthenium nitrosochloride, $Cs_2\overset{IV}{R}uCl_5NO$, which had been boiled some time with sulphuric acid, and which might be supposed to contain the nitrososulphate. It was hoped to reduce the nitroso group and split it off as ammonia, leaving trivalent ruthenium in the presence of sulphuric acid and cesium sulphate, the most favorable condition for alum formation. No sign of alum was found, nor did the electrolyzed solution show reaction for trivalent ruthenium. A considerable quantity of ruthenium tetroxide, RuO_4, was given off. This was probably owing to oxidation at the positive pole, some of the ruthenium solution having penetrated the diaphragm into the sulphuric acid which surrounded the positive pole. The formation of ruthenium tetroxide by electrolytic oxidation has not been pre-

[1] Since the above was in type, a further article by Piccini has appeared in the *Zeitschrift für anorganische Chemie*, 17, 361, describing the formation of the cesium manganese alum by electrolytic oxidation, in a method apparently like that described in this paper. No particulars regarding current, etc., are given. This would seemingly settle the question of the trivalence of manganese in manganic salts. Attention is called, as in our paper, to the advantage in using rubidium and cesium compounds where it is desired to obtain difficultly crystallizable compounds. Piccini's result renders it probable that the few octahedra obtained in our rubidium manganese experiment were really rubidium manganese alum; he also found his alum contaminated by aluminum from the diaphragm.

viously noticed. Further experiments with other ruthenium compounds are being carried on.

WASHINGTON AND LEE UNIV.,
July 1, 1898.

ON THE DETERMINATION OF UNDIGESTED FAT AND CASEIN IN INFANT FECES.[1]

BY HERMAN POOLE.

Received August 29, 1898.

LAST summer I had the honor of presenting to the Society a paper on "Methods of Determining Fat and Casein in Feces."[2] In that paper I mentioned the method I had adopted in the investigation I was then engaged in, and stated why the methods previously used did not give me satisfactory results. This paper may be considered as a sequel to that one, or perhaps more correctly, a résumé of the work I have done on the subject to this time. The methods given in the paper cited were used substantially as there given throughout all the cases, no better one having been suggested; in fact, my requests for other methods met with no response at all, showing that but little work had been done directly on this line.

The methods of analysis used may be briefly stated as follows: The feces were carefully removed from the containers as well as possible and thoroughly mixed, if practicable. A portion of this was then weighed out and dried in an air-bath at 90° C. for one hour, and afterwards at 105° to 110° C. for two or three hours or until of constant weight. A portion of this dried residue was then treated with ether in a Soxhlet extraction apparatus to extract the fat and other substances soluble in ether. The extract so obtained was evaporated at 100° till dry and usually weighed. This weighing was not done in every case as it had no important bearing on the aim of the investigation, which concerned the undigested fat and casein only. After drying, the extract was saponified with alcoholic potash, a small portion generally remaining undissolved. Water was then added and the whole boiled till the alcohol had been expelled. Practically this was carried on until the mass was nearly dry, water having

[1] Read at the Boston Meeting of the American Chemical Society, August, 1898.

[2] This Journal, 19, 877.

been added during the boiling. The solution was then diluted with water and filtered.

The cholesterol being soluble in ether was then taken up by agitation in a separatory globe with that solvent. On allowing the mixture to rest the two liquids separated readily, especially after a reagitation. The treatment with ether was generally repeated once, occasionally twice. The second repetition was hardly necessary, as only traces were taken up.

The solution thus freed from cholesterol was evaporated nearly dry, dissolved with water, and the fat acid determined as usual by precipitation with mineral acid, collecting, and weighing. The solution was usually clear enough without filtration.

In many cases the cholesterol solution in ether was evaporated and that body determined. As this was only of minor interest and not germane to the investigation, it was done only when it did not interfere with other work. No regular ratio of the fat and cholesterol could be established.

The solid residue from the ether extraction was treated successively with water and alcohol and then dried at 100° C. This dried residue was afterwards digested in a mixture of equal parts of water and hydrochloric acid for some ten or twelve hours at a temperature of about 60° C. This dissolved the casein and at the same time decomposed the earthy fat acid compounds, and, on cooling, a collection of fat acid was always found. No attention was paid to this fat acid as, being in combination with bases, it was considered to have been digested or changed in the system, and only undigested fat was sought. This fat acid was quite hard and usually, though not always, nearly white in color.

After cooling the solution of casein and filtering, it was evaporated to dryness and the nitrogen determined by the Kjeldahl method. The casein was estimated as being $\frac{100}{15}$ of the nitrogen so determined.

The results obtained are shown in the accompanying table, which contains the results from most of the cases examined :

CASE I.

	Reaction.	Quantity. Grams.	Water. Per cent.	Fat.[1] Per cent.	Cholesterol.[1] Per cent.	Casein.[1] Per cent.
1	Acid.....	28.0	67.7	17.52	11.25	3.28
2	Acid.....	23.0	75.0	18.88	8.40	4.24
3	Acid.....	26.0	73.3	14.23	5.11	4.35
4	Acid.....	30.0	76.1	9.86	6.50	5.02
5	Faint acid	29.0	68.8	7.11	3.68	3.67
6	Nearly neutral..	10.8	69.9	12.65	5.92	3.52
7	Neutral	35.7	65.0	9.26	6.24	...
8	Neutral	38.6	65.0	8.54	7.61	3.11
9	Faint acid.....	62.5	55.0	5.53	5.01	2.87
10	Faint acid.....	42.6	71.5	8.63	5.17	...
11	Faint acid.....	15.8	63.2	8.55	4.99	3.81
12	Very faint acid .	51.8	51.2	...	2.57	3.16
13	Neutral	33.0	61.2	6.44	3.21	4.77
14	Acid.....	21.0	75.0	11.68	7.50	6.00
15	Neutral	18.4	70.6	13.57	4.43	6.00
16	Very faint acid .	29.0	69.3	11.06	5.81	7.97
17	Very faint acid .	23.4	63.0	9.86	8.91	5.19
	Average	27.96	67.2	10.90	6.39	5.03

CASE II.

1	Acid.....	9.8	77.95	24.14	22.76	8.24
2	Faint acid.....	5.2	60.00	12.98	7.69	7.65
3	Faint acid.....	7.7	72.83	14.76	15.31	7.54
4	Faint acid.....	33.44	65.14	8.84	8.11	5.81
5	Faint acid.....	19.36	70.20	10.57	6.63	3.68
6	Neutral	6.6	65.66	8.74	10.11	4.48
7	Acid.....	12.6	69.18	10.67	9.14	6.04
8	Faint acid.....	8.76	74.86	11.27	20.11	4.97
9	Acid.....	10.56	75.18	13.09	20.85	7.21
10	Faint acid.....	9.32	76.14	14.44	....	8.95
11	Faint acid.....	3.12	79.69	22.11	....	...
12	Faint acid.....	17.13	71.84	12.18	15.10	8.59
	Average	11.92	71.57	14.47	13.58	6.65

VARIOUS SAMPLES.

1	Faint acid.....	about five grams	78.40	9.17	12.80	16.39
2	Faint acid.....		75.45	19.81	10.91	12.22
3	Acid.....		53.25	8.98	16.15	5.68
4	Faint acid.....		46.55	9.57	4.85	6.31
5	Faint acid.....	20.0	73.00	22.60	8.25	13.15

[1] These are calculated on the dry material.

The reaction with litmus was almost uniformly acid, although seldom strong enough to admit of determination. In a few cases no action was noticed and in a very few a slightly alkaline reaction was observed. It is possible that these alkaline cases may have been due to decomposed urine, all the samples being old (*i. e.*, more than one day).

The quantity excreted varied considerably, but the quantity as given in the table does not show the actual quantity voided. It simply shows the amount available for analysis, and in many instances this was only a small percentage of the entire amount, but from physical reasons it was impossible to obtain any more in a clean condition, free from extraneous substances. The quantity column of Case I fairly represents the actual amounts per day.

The amount of moisture varied considerably and its determination was generally of no use except as a means of reducing the subsequent results to a dry basis. Many of the samples were fairly fresh and in such cases a percentage of about seventy was attained. Departures far from this amount occurred only in old and partially dried samples.

The quantity of fat, casein, and cholesterol varied considerably. Not only is a large variation noticeable between the different individuals but also in the same case from day to day. There seems to be no relation existing between the proportions of these three, except that generally a large amount of fat is accompanied by a correspondingly large amount of casein. This could be expected, as the presence of an increase in one would be caused by a derangement of the intestinal canal and should have an effect on the other also. This is quite evident in the latter part of the data from Case I. In this instance the removal of the child to the country had a marked and unmistakable effect on the feces; still, the child was reported in good health.

Incidentally, it may be mentioned that the characteristic odor of adult feces was entirely wanting. It showed itself in one instance only, and this case was dismissed for that reason. Subsequent investigation showed that the child had been fed on a mixed diet. Indol and skatol were looked for but not formed except in the case just mentioned.

All the children were fed on the same kind of milk, and given approximately the same quantities per day. This milk was not a single cow's milk but a milk prepared by the "Gaertner Mother Milk" method from the average milk of a large number of cows, and care was taken to have the milk as near as possible of the same composition. The analysis of the milk was approximately

	Per cent.
Fat	3.05
Casein	2.09
Lactose	6.00

Specific gravity, 1.0275.
Reaction, faintly alkaline.

The milk was sterilized perfectly and did not become sour after standing exposed for three days.

Each child consumed from one to one and one-third liters daily and hence ingested

	Grams.
Fat	30.5 to 40.67
Casein	20.9 to 27.87
Lactose	60.0 to 80.0

Cases I and II were well cared for throughout the investigation and the results obtained may be considered as reliable as possible from such cases. The others are given to show the range of results obtained, but from reasons beyond the control of the investigation, modifying influences were present; and, while the analytical results are individually correct, the connection between the food ingested and the excreta cannot be traced.

ELECTRIC FURNACES FOR THE 110-VOLT CIRCUIT.[1]

By Nevil Monroe Hopkins.

Received August 29, 1898.

IT occurred to the writer in wiring a couple of experimental arc lamps across the feeders of an incandescent lighting system, that a laboratory electric furnace could be operated on a series carbon plan, without disturbing the protecting fuses of the circuit. The idea of focusing a pair of arcs within a small crucible, or furnace, using only the amount of resistance located in the tops of typical series lamps, proved, however, to be unsatis-

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

factory, the current absorbed becoming abnormal, upon introducing a charge for fusion, when its character embodied fair electrical conductivity. To obviate this difficulty, as well as to compensate for the lowering of resistance due to eddy currents between the poles when run in combination with a charge rich in carbon, or graphite, as in the making of calcium carbide, a third pair of electrodes was placed in series, together with a variable rheostat in place of the resistance wire of the lamps. With this arrangement, calcium carbide was readily prepared on a laboratory scale, using only a twelve ampère fuse wire in each leg of the feeding conductors, and allowing the separation of the electrodes through a distance of three and one-half inches. The charge of lime and coke was finely ground together in an iron mill before feeding into the furnace, insuring a homogeneous body. It may be of interest to state in connection with this work that lime and charcoal are poorly adapted for the purpose, the charcoal, because of its floury nature, oxidizing rapidly away from the lime without combining with it. Fig. 1 illus-

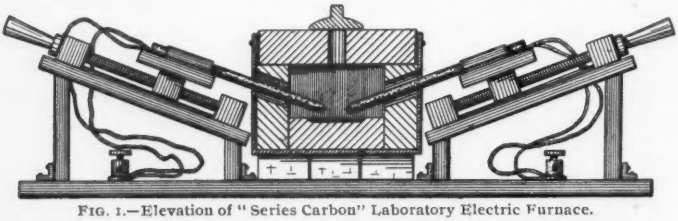


FIG. 1.—Elevation of "Series Carbon" Laboratory Electric Furnace.

trates the "series carbon" furnace in elevation and partial section, showing a simple construction. Fig. 2 gives a plan view

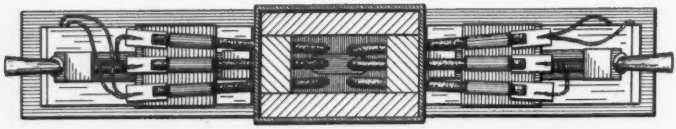


FIG. 2.—Plan View of Furnace with Cover Removed.

of the apparatus with the cover of the furnace proper removed. This furnace, which consists of an iron shell, lined with fire-clay, should not be over twelve inches long if intended

for use with ordinary electric light carbons, because of their limited reach. The screw mechanism of this "plant" is readily put together by cutting into sections a large furniture-maker's clamp, using the unthreaded portions for the end bearings, and the two threaded sections for the center pieces, which travel back and forth. The carbon electrodes are conveniently mounted on a block by means of tightly-fitting brass tubes, attached in turn with staples or "straps" and screws. Contact is made with the ends of the carbons by pushing brass spring jacks under their ends, to which the connections are soldered. These pieces of spring brass allow of the rapid adjustment of the carbon pencils, or their removal when too short for further use. To start the furnace, when properly connected, it is necessary to feed the electrodes into the furnace until they are all in good contact, and strike the wooden incline planes with a mallet, which causes the ends of the carbons to vibrate or rub together, and make good contact. When the arc has once formed the furnace may be handled like an ordinary single carbon equipment. The method of wiring is given in Fig. 3, where M represents the

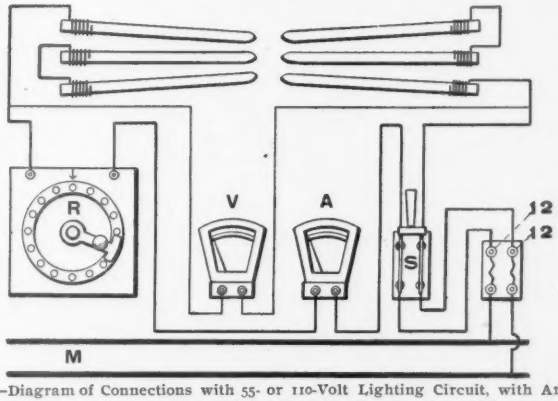


FIG. 3.—Diagram of Connections with 55- or 110-Volt Lighting Circuit, with Ammeter and Voltmeter Arranged for Studying the Behavior of Bodies within the Arc.

main feeders, with a fuse block connected at the right, carrying a pair of twelve ampère fuses. The knife switch S is an important feature, and should be within easy reach of the furnace. The ammeter A and the voltmeter V are included as a matter of

interest, and afford a ready means of watching the behavior of different bodies with the arcs. The variable rheostat, R, completes the equipment, which must also be in easy reach of the furnace. In order to avoid annoyance from intermediate fuses, the apparatus should be connected, as near the meter as possible, if the current is sold on this plan. Should one of the twelve ampère fuses melt out, it should be replaced by another of the same capacity, and a little more resistance put in by means of the variable rheostat. Of course, fifteen and twenty ampère fuses may be used if desired, the twelve ampère size being about the smallest for the fusion of compounds possessing carbon as one of the ingredients. Should the variable rheostat at hand prove of too low a resistance for the preservation of the twelve ampère fuses, a second rheostat may be placed in series with it, although with the triple arc arrangement this will seldom be necessary. Fig. 4 illustrates a method for using a sin-

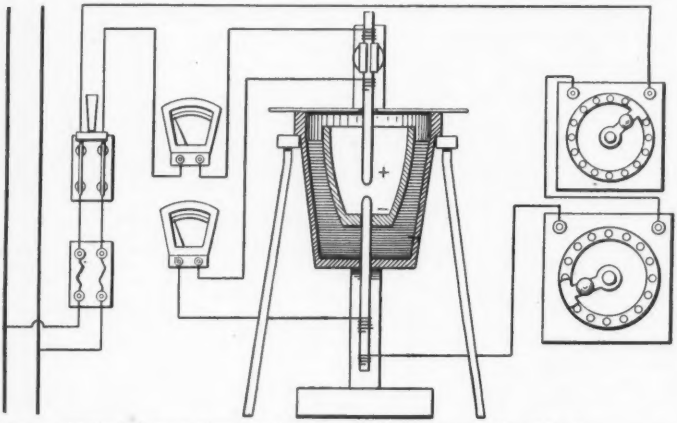


FIG. 4.—Method of Using Single Carbons for making Alloys and Small Fusions. 55- or 110-Volt Circuits.

gle pair of carbons for making alloys and other small fusions. Here, at least, two large rheostats will be necessary, and fuses of larger capacity must be employed. The small crucible is drilled through the bottom, receiving the lower electrode with a tight fit. The outer casing of the furnace in this instance consists simply of a large flower-pot filled in with some poor conductor of

heat. The ammeter gives the total current absorbed, and the voltmeter the electromotive force at the arc. With this simple arrangement, copper and brass are easily melted, as well as iron and steel. As to the adjustment of the carbons, it is only necessary to feed the upper one down a fraction of an inch every two or three minutes. Should rheostats not be at hand, a bank of thirty-two C. P. lamps arranged in multiple and joined in with the furnace, answer the purpose for smaller fusions, and for metals possessing lower melting-points. By using ten 32 C. P. lamps in parallel, a good arc may be maintained, sufficient for small reductions, etc. Should three of these "flower-pot" furnaces be placed in series, the principle of the large furnace will obviously be brought into play, if some means is devised for controlling the upper carbons simultaneously.

ON TETRAPHENYLMETHANE.[1]

By M. Gomberg.

Received August 29, 1898.

About a year ago[2] I reported a method by which small quantities of tetraphenylmethane were obtained, a substance which it had been proved impossible to prepare by the usual reactions.[3] The method consisted in oxidizing triphenylmethanehydrazobenzene to the corresponding azo-compound, and heating the latter to 110°–120° C. The reactions can be summarized by the following equations:

(1) $(C_6H_5)_3CBr + 2C_6H_5NHNH_2 = (C_6H_5)_3C.NH.NH.C_6H_5 + C_6H_5NHNH_2.HBr.$

(2) $(C_6H_5)_3C.NH.NH.C_6H_5 + O = (C_6H_5)_3C.N:N.C_6H_5 + H_2O.$

(3) $(C_6H_5)_3C.N:N.C_6H_5 = N_2 + (C_6H_5)_3C.C_6H_5.$

Unfortunately, the yield was very small, and even then the substance could be obtained only with difficulty.

The work has since been subjected to a revision, but with no better results in so far as the yield of tetraphenylmethane is concerned.

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *Ber. d. chem. Ges.*, 30, 2043, *1897*.

[3] Haemilian, *1874: Ber. d. chem. Ges.*, 7, 1209; Friedel and Crafts: *Compt. rend.*, *1877*, 153; *Ann. chim. phys.*, *1884*, 1, 497; E. and O. Fischer, *1878: Ann. Chem.* (Liebig), 194, 254; Magati, *1879: Ber. d. chem. Ges.*, 12, 1468; Schwartz, *1881: Ber. d. chem. Ges.*, 14, 1523; Waga, *1894: Ann. Chem.* (Liebig), 282, 330; Weisse, *1895: Ber. d. chem. Ges.*, 28, 1537.

The method of oxidizing the hydrazo- to the azo-body has been greatly improved, and was found to be of general application for the preparation of azo-derivatives of this class.[1]

A mere elementary analysis is not sufficient to establish the composition of tetraphenylmethane, as the percentage of carbon and hydrogen is almost the same as that in triphenylmethane, and in other phenylated methane and ethane derivatives. A redetermination of the *molecular weight* seemed therefore very desirable, inasmuch as only about one-tenth gram of the substance was at my disposal for the first determination. The amount employed this time was again small, about 0.124 gram. It was nearly all recovered, and used for the preparation of a nitro-compound, furnishing, *quantitatively*, a tetranitro-derivative.

It has been shown by V. v. Richter[2] that the accumulation of nitro-groups in phenylmethanes imparts to these compounds sufficient negative character, so that they form salts with caustic potash, and especially with sodium ethylate. These salts are intensely colored, usually dark violet. They are formed by the replacement of sodium for the methane-hydrogen, giving, for example,

$$[C_6H_3(NO_2)_2]_2CHNa,\quad C_6H_4NO_2CHNa.CN,\quad (C_6H_4NO_2)_3CNa.$$

This reaction with triphenylmethane is exceedingly characteristic,—a fragment of a crystal of trinitrotriphenylmethane dissolves in sodium ethylate with a fine violet color.[3] The nitro-derivative, however, obtained from tetraphenylmethane, does not give any colored salts with caustic alkali or with sodium ethylate, even on heating. This is strong corroborative evidence of the constitution of tetraphenylmethane, showing that all the four hydrogen atoms in methane must have been replaced.

When the nitro-compound is treated with acetic acid and zinc dust, it shows the characteristic fuchsin reaction. Three to four milligrams suffice for this test. Lack of material prevented from fully identifying the dye as pararosanilin, since all this work, including the molecular weight determination, was performed on about two-tenths gram of tetraphenylmethane. An alcoholic

[1] See next paper : This Journal, 20, 780.

[2] *Ber. d. chem. Ges.*, 21, 2470, 2475, *1888*.

[3] Trinitrotriphenylcarbinol gives the same reaction on warming.

solution of the dye gave the same absorption spectrum as pararosanilin, prepared under exactly similar conditions directly from triphenylmethane. The formation of a rosanilin dye, involving, as it does, a splitting off of a *p*-amidophenyl group, is not so very surprising, when we consider the great tendency for the formation of such dyes under the most varied conditions. The historic reaction of Hofmann,[1] which led to the discovery of the rosanilin group, may be cited in this connection. By the action of anilin upon carbon tetrachloride, he obtained not the expected tetraamidotetraphenylmethane, $(C_6H_4NH_2)_4C$, but *p*-rosanilin:

$$CCl_4 + 3C_6H_5NH_2 = \begin{matrix} C_6H_4NH_2 \\ C_6H_4NH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6H_4 \\ | \\ NH \end{matrix} + 4HCl.$$

The formation of the pararosanilin or a rosanilin-like dye, from the tetranitrotetraphenylmethane shows, that at least three nitrogen groups are in *para* position to the central carbon atom. And it is quite probable that the fourth nitro-group also occupies the para position.

EXPERIMENTAL PART.

Triphenylmethaneazobenzene, $(C_6H_5)_3C.N:N.C_6H_5$.—The hydrazo-derivative was obtained by the action of phenylhydrazine upon triphenylbrommethane, in an ethereal solution, with a yield of seventy to eighty per cent. of the theoretical quantity. It has been stated before,[2] that of all oxidizing agents tried, amyl nitrite gave the best results in oxidizing the hydrazo to the azo-body. But even with amyl nitrite the oxidation sometimes goes too far, especially if larger quantities are worked with at one time. In such cases a considerable amount is oxidized to triphenylcarbinol, and a portion is entirely decomposed. It was now found that the substitution of nitrous acid gas for amyl nitrite gives much better results. The hydrazo-compound is dissolved in ether, and nitrous acid gas is passed in, until the solution turns milky and shows signs of boiling. The solution is allowed to stand about half an hour. On concentrating, the azo-derivative separates in large, bright yellow crystals, melting at 110°–112° C. The yield is very satisfactory.

1 *Compt. rend.*, 47, 492.
2 *Ber. d. chem. Ges.*, 30, 2045, *1897*.

Seventeen grams of the hydrazo-body furnished by this method 14.5 grams of the azo-compound.

Action of Bromine.—When bromine is added to a solution of the azo-compound in chloroform, a heavy dark oil separates, which, after standing for some time, changes to a crystalline perbromide on stirring. The addition of a little petroleum ether hastens greatly the crystallization. The crystals obtained in this way were filtered, washed with a little chloroform and petroleum ether, and rapidly dried *in vacuo*. The inner portion, showing no decomposition by loss of bromine, was analyzed. The "perbromine" was estimated by suspending weighed samples of the perbromide in a solution of potassium iodide in water, and titrating the iodine with a standard solution of sodium thiosulphate.

	Calculated for $(C_6H_5)_3CBr.Br_2$.	Found.
Perbromine.....	55.33	54.85

When the perbromide is exposed to the air, it loses bromine, and leaves a white powder, which consists for the most part of triphenylbrommethane. On boiling the perbromide with alcohol, triphenylcarbinol was obtained (melting-point 158° C.)

The existence of such a perbromide is made quite probable by the existence of an analogous periodide.[1] Indeed, triphenylbrommethane itself, treated in a chloroform solution with bromine, gives also a crystalline perbromide, with similar properties and of the same composition as the perbromide described. This reaction is to be further studied.

Tetraphenylmethane, $\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}$.—Triphenylmethaneazobenzene behaves in many respects like a true mixed fatty-aromatic azo-body. Thus, when heated to its melting-point, it decomposes with evolution of nitrogen, the amount of gas given off being quantitative.[2] The decomposition this time has been carried out as follows: About ten grams of pure clean sand, which had been thoroughly washed with benzene, was placed in a small flask and heated in an oil-bath to 110°–120° C. Fifteen grams of the finely powdered azo-compound was then gradually

[1] This Journal, **20**, 790.

[2] *Ber. d. chem. Ges.*, **30**, 2045, *1897*.

added, a little at a time, with constant stirring. When no further evolution of gas could be noticed, the mass was extracted with hot benzene, filtered, and the solution concentrated on the water-bath. The residue consisted of a very thick, dark mass. This was divided into two portions. To one portion a very little benzene was added, and the sirupy mixture was allowed to stand until crystallization set in, in about four or five days. The small crop of crystals was separated from the mother-liquid by filtration on a pump and washed on a porous plate with a little petroleum ether. It was then recrystallized several times from small quantities of hot benzene, until absolutely white and of a constant melting-point. The yield of the pure substance was a little over two-tenths gram. The molecular weight determination was made with this material. The mother liquor, after several weeks' standing, furnished another crop of the tetraphenylmethane, which, when purified, will probably amount to about one-tenth gram.

The second portion of the original dark mass, as obtained from the decomposition of the azo-compound, was subjected to distillation *in vacuo*, at fifteen to eighteen mm. The temperature of the metal-bath was allowed to go up to 320° C. The distillate, which amounted to about one-half of the quantity taken, presented a dark-yellow viscous mass. On standing, a small quantity of triphenylmethane crystallized out. The rest, as well as the residue in the distilling flask, could not be brought to crystallization. No diphenyl or diphenylmethane could be detected.

Molecular Weight.—As naphthalene had given very good results in the first determination, the same solvent was chosen again for the cryoscopic method. It has the advantage when small quantities of the substance are at one's disposal, because of its high constant. Trials with triphenylmethane had shown that the naphthalene was pure, and that very good results could be obtained with this solvent.

Solvent: Benzene.

Formula: $\frac{69 \times p}{d} = m.$

p = per cent. of substance in solvent.

d = depression.

Tetraphenylmethane, $m = 320$.

Solvent. Gram.	Substance. Gram.	p.	d. °C.	m.
9.427	0.1239	1.314	0.285	318

The tetraphenylmethane as now obtained has been found to agree in all properties with the substance previously reported. It is insoluble in ether, chloroform, petroleum ether, glacial acetic acid. Fairly soluble in hot benzene, but very little in the cold. It crystallizes from benzene in white, glistening needles. The melting-point, determined this time in a closed dish and with a normal thermometer, was found to be 272° C. instead of 267.5° C., as given before.

Recovery of the Tetraphenylmethane.—Nearly all the quantity employed in the determination of the molecular weight was recovered. The naphthalene was placed in a crystallizing dish and sublimed off at the lowest possible temperature. The residue was boiled out first with a little petroleum ether, and then thoroughly washed with ether. The white silky residue showed the correct melting-point of tetraphenylmethane, and amounted to 0.1075 gram.

TETRANITROTETRAPHENYLMETHANE, $(C_6H_4NO_2)_4C$.

The quantity of tetraphenylmethane recovered from naphthalene after the determination of the molecular weight, was nitrated. The nitration was done according to the method employed by E. and O. Fischer[1] for the preparation of *para*-trinitrotriphenylmethane. The hydrocarbon was added in small quantities to two cc. of nitric acid (sp. gr. 1.50), cooled in ice-water. The substance dissolved very readily. The bright yellow solution was allowed to stand about fifteen minutes. On the addition of water the nitro-compound separated in white minute crystals, without the slightest trace of any oily, sticky by-products, as is always the case when triphenylmethane is nitrated. The crystalline precipitate was separated by means of a pump, thoroughly washed with water, alcohol, and finally with a little ligroïn, and dried *in vacuo* over sulphuric acid. The yield was 0.166 gram, while theoretically 0.107 gram of tetraphenylmethane should yield 0.1669 gram of the tetranitro-derivative.

The substance was analyzed with the following results:

0.1417 gram gave 14.8 cc. nitrogen at 24° and 737 mm.

[1] *Ann. Chem.* (Liebig), 194, 254.

	Calculated for $(C_6H_4NO_2)_4C$.	Found.
N	11.20	11.68

The nitro-derivative, as already mentioned, consisted of minute, white, needle-like crystals. It is insoluble in ether, petroleum ether, alcohol; insoluble in cold glacial acetic acid, and only slightly when heated. It is somewhat soluble in hot benzene and hot chloroform, from either of which solvents it can be obtained in a nice crystalline form. It begins to darken at about 268° C., and melts at 275° C.

Unlike the trinitrotriphenylmethane, or the trinitrotriphenylcarbinol, it does not dissolve in sodium ethylate, nor does it give any coloration with it even on heating. The non-formation of colored alkali salts, as well as the high melting-point, show the absence of any nitrotriphenylmethane.

The nitration of the hydrocarbon has been repeated several times on small quantities, five to ten milligrams, of the original tetraphenylmethane, which had not been employed for the determination of the molecular weight, but the results were in every respect identical with those described above.

Reduction to a Rosanilin Dye.—About five milligrams of the nitro-compound were dissolved in boiling glacial acetic acid, and zinc dust gradually added in small quantities. On the first addition of the zinc the solution turned a bright red, and the reduction to a colorless base required considerable zinc dust and boiling. The solution was diluted with water, filtered from the excess of zinc dust, treated with excess of ammonia, and the precipitated colorless leuco-base was filtered and washed. The base was then gently ignited with a few drops of concentrated hydrochloric acid on a platinum foil, according to the method of E. and O. Fischer[1] for triphenylmethane. The characteristic fuchsin color so developed could not be distinguished at any stage from that produced by the reduction-product of *p*-trinitrotriphenylmethane. The two were reduced in about the same quantities and under the same conditions. The two dyes were dissolved in about the same amount of alcohol, and when examined spectroscopically, gave about the same absorption bands.

Lack of material prevented me from establishing the identity of the dye.

[1] *Ann. Chem.* (Liebig), 194, 273.

The subject will be continued, and it is hoped that perhaps larger quantities of tetraphenylmethane will be obtained by the action of triphenyliodomethane upon mercury-diphenyl.

ANN ARBOR, MICHIGAN.

HYDRAZO- AND AZO-DERIVATIVES OF TRIPHENYLMETHANE.[1]

BY M. GOMBERG AND A. CAMPBELL.

Received August 29, 1898.

ONE of us has recently[2] described a method by which small quantities of tetraphenylmethane were obtained. The method involved the synthesis of triphenylmethaneazobenzene, which was obtained by the oxidation of the corresponding hydrazo-derivative. The azo-body, on being heated to 110°–120° C., loses nitrogen, and furnishes, among other products, tetraphenylmethane.

The present work was undertaken with the hope of obtaining substitution derivatives of tetraphenylmethane, by subjecting substituted azo-compounds of triphenylmethane to the same treatment as the simple azo-compound itself. For the present, we shall only give a description of the hydrazo- and azo-bodies, which have been prepared by us in connection with this work.

The number of mixed azo-bodies, *i. e.*, those containing an aliphatic and an aromatic radical, is quite limited. A few have been prepared by E. Fischer and Ehrhard,[3] and Tafel[4] by the oxidation of the corresponding hydrazo-derivatives. The principal method of preparation is, however, by combining aromatic diazo-salts with aliphatic compounds. This reaction, first worked out by V. Meyer[5] on nitroethane, has since been extended to a large number of such aliphatic compounds, as contain a (CH_2)-group linked to some negative groups. Nitro-compounds, malonic ester, aceto-acetic ester, etc., give such bodies. The constitution of all these so-called azo-bodies has, however, recently been called into question by the work of Japp

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] *Ber. d. chem. Ges.*, **30**, 2043; This Journal, **20**, 773.

[3] *Ann. Chem.* (Liebig), **199**, 328, *1879*; *Ber. d. chem. Ges.*, **29**, 793, *1896*.

[4] *Ber. d. chem. Ges.*, **18**, 1742, *1885*.

[5] *Ber. d. chem. Ges.*, **8**, 751, *1875*; **18**, 1742, *1885*.

and Klingmann,[1] and others,[2] who have shown, for many compounds, the identity of the azo-formula, $R.N:N.CH$, with that of the hydrazo-formula, $R.NHN:C$. This has opened the question, as to whether all the mixed azo-compounds, obtained by the above reaction, are not after all hydrazones. An intramolecular change of this nature can, of course, take place only in such compounds as contain a (CH)- or (CH_2)-group. If this view be correct, then the number of mixed azo-bodies is indeed very small. The phenylazoisovaleric acid of Prentice[3] might be mentioned in this connection as being a true mixed azo-compound.

We have found that the reaction of phenylhydrazine with triphenylbrommethane is of general application. All hydrazines, so far as tried, react very readily with this bromine compound, and give hydrazo-bodies, which furnish, on oxidation, with more or less readiness, the desired azo-derivatives. The following hydrazines have been tried: Paratoluylhydrazine, orthonitrophenylhydrazine, metanitrophenylhydrazine, paranitrophenylhydrazine, metachlorphenylhydrazine, parachlorphenylhydrazine, metabromphenylhydrazine, and α-naphthylhydrazine.

These hydrazo-bodies are well crystallized; they are colorless, with the exception of those containing the nitro-group, which are colored yellow to reddish-brown. They are soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroïn. They oxidize very readily on exposure to the air, thus resembling more the aromatic than the purely fatty hydrazo-bodies. They are weak bases and form salts with dry hydrochloric, oxalic, picric, and other acids.

The azo-derivatives are also well crystallized compounds, colored from yellow to orange. They are very soluble in benzene and chloroform, less soluble in ether, alcohol, and acetic acid, and only sparingly soluble in ligroïn. They all give off their

[1] *Ber. d. chem. Ges.*, 20, 3398, *1887*; *Ann. Chem.* (Liebig), **247**, 190.

[2] R. Meyer: *Ber. d. chem. Ges.*, **21**, 118, *1888*; **24**, 1241, *1891*; V. Meyer, 1888: *Ber. d. chem Ges.*, **21**, 11; Baeyer and Claisen: *Ibid.*, 1697; **25**, 746, *1892*; v. Pechmann, 1892: *Ber. d. chem. Ges.*, 25, 3190.

[3] *Ann. Chem.* (Liebig), **292**, 272.

nitrogen on being heated, thus resembling the simple triphenylmethaneazobenzene. The liberation of nitrogen is quantitative, and takes place at temperatures ranging from 103.5° to 118.5° C. The relative position of the chlorine or the nitro-group seems to exert no particular influence upon the temperature at which the azo-body decomposes.

Molecular weight determinations show them to be monomolecular.

When dissolved in chloroform and treated with bromine, they form crystalline perbromides. These have not yet been analyzed.

EXPERIMENTAL PART.

ACTION OF PARATOLUYLHYDRAZINE.

Triphenylmethanehydrazoparatoluene, $(C_6H_5)_3C.NH.NH.C_6H_4.CH_3$.—Paratoluylhydrazine[1] (two molecules) was dissolved in dry ether and slowly added, with stirring, to a cold ethereal solution of triphenylbrommethane (one molecule). The solution was allowed to stand protected from the air until the precipitate of toluylhydrazine hydrobromide separated out. The reaction is represented by the following equation:

$$(C_6H_5)_3CBr + 2H_2NHNC_6H_4CH_3 = (C_6H_5)_3C.NH.NH.C_6H_4.CH_3 + CH_3.C_6H_4NHNH_2HBr.$$

Upon filtering off the precipitate of toluylhydrazine hydrobromide and concentrating the ethereal solution, white crystals of the hydrazo-body were obtained. They were recrystallized from ether and analyzed with the following results:

0.212 gram gave 15 cc. nitrogen at 20° and 736.6 mm.

	Calculated for $C_{26}H_{27}N_3$.	Found.
N	7.69	8.02

This hydrazo-derivative is readily oxidized on exposure to the air, especially in an alcoholic solution. It is a weak base, forming salts with dry hydrochloric, oxalic, picric, and other acids. It is soluble in benzene, chloroform, less soluble in alcohol and ether, and insoluble in water and ligroïn. It melts with decomposition at 157° C.

Triphenylmethaneazoparatoluene, $(C_6H_5)_3C.N:N.C_6H_4.CH_3$.—After trying numerous oxidizing agents, such as potassium per-

[1] E. Fischer, 1876: *Ber. d. chem. Ges.*, 9, 890.

manganate, ferric chloride, mercuric oxide, and amyl nitrite, the last named reagent was found to give the best results.[1] The hydrazo-body was suspended in ether and the calculated quantity of amyl nitrite added. A drop of acetyl chloride was sufficient to start the action. The hydrazo-body was gradually changed to the azo, which dissolving in the ether produced a deep yellow solution. Upon concentration, long yellow needles of the azo-compound separated. The reaction is as follows:

$$(C_6H_5)_2C.NH.NH.C_6H_4.CH_3 + O =$$
$$(C_6H_5)_2C.N : N.C_6H_4.CH_3 + H_2O.$$

Recrystallized from methyl alcohol the compound gave the following results upon analysis:

0.1505 gram gave 0.4725 gram carbon dioxide + 0.083 gram of water.

0.263 gram gave 18 cc. nitrogen at 21° and 731.5 mm. when heated to 150° C.

	Calculated for $C_{26}H_{22}N_2$.	Found.
C	86.18	85.79
H	6.07	6.15
N	7.73	7.70

The molecular weight determination furnished the following results:

Triphenylmethaneazoparatoluene, $C_{26}H_{22}N_2 = 362$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18.589	0.4563	0.42°	292

The azo-compound is soluble in benzene, chloroform, ether, less soluble in alcohol, and only sparingly soluble in ligroïn. It melts at 103.5° C. with evolution of nitrogen. An attempt has been made to determine the products of decomposition. The substance was mixed with copper-bronze, to facilitate decomposition, and heated to 120° C. The reaction which took place was apparently a complicated one, and as yet satisfactory results have not been obtained.

ACTION OF NITROHYDRAZINES.

Triphenylmethanehydrazoorthonitrobenzene, $(C_6H_5)_2C.NH.NH.$-

[1] Recent experiments show that nitrous acid gas, passed into an ethereal solution of the hydrazo-derivatives of triphenylmethane, gives the best results in oxidizing them to the corresponding azo-compounds. This Journal, **20**, 775.

$C_6H_4NO_2(o)$.—Orthonitrophenylhydrazine[1] was allowed to react with triphenylbrommethane under conditions similar to those in the preparation of triphenylmethanehydrazoparatoluene. Upon concentrating the ethereal solution brownish crystals of triphenylmethanehydrazoorthonitrobenzene separated. The yield is quantitative. Recrystallized from ether it was analyzed with results as follows:

0.1816 gram gave 17.4 cc. nitrogen at 22.5° and 741.7 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
N	10.63	10.86

This hydrazo-compound is soluble in benzene, chloroform, less soluble in ether and alcohol, and is insoluble in ligroïn. It forms salts with dry acids, melting-point 168° C. It oxidizes partially to the azo-compound on exposure to the air.

Triphenylmethaneazoorthonitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2(o)$.—This compound is prepared from the corresponding hydrazo-body by oxidation with amyl nitrite or nitrous acid gas in an ethereal solution. Recrystallized from methyl alcohol it is obtained in bright canary-yellow needles, perfectly pure.

0.261 gram gave 0.7273 gram carbon dioxide + 0.1201 gram of water.

0.1437 gram gave 13.5 cc. nitrogen at 22° and 739 mm.

	Calculated for $C_{25}H_{19}N_3O_2$.	Found.
C	76.33	75.98
H	4.83	5.11
N	10.67	10.62

The compound is soluble in benzene, chloroform, ether, less soluble in alcohol, and sparingly soluble in ligroïn. Melting-point 116° C. It forms a crystalline perbromide.

Molecular weight determination:

Triphenylmethaneazonitrobenzene, $C_{25}H_{19}N_3O_2 = 393$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
18 598	0.6245	0.49°	338

Triphenylmethanehydrazometanitrobenzene, $(C_6H_5)_3C.NH.NH.C_6H_4NO_2(m)$.—Metanitrophenylhydrazine[2] is treated with triphenylbrommethane, as in the case of the corresponding ortho-

[1] Bischler, 1889: *Ber. d. chem. Ges.*, **22**, 2801.

[2] Bischler and Brodsky, 1889: *Ber. d. chem. Ges.*, **22**, 2809.

body. The hydrazo-compound crystallizes out on concentrating the solution in reddish-brown crystals. Recrystallized from ether it gave the following results:

0.2374 gram gave 0.6528 gram carbon dioxide + 0.1151 gram of water.

0.2342 gram gave 22.6 cc. nitrogen at 22° and 741.7 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
C	75.37	75.11
H	5.28	5.34
N	10.63	10.96

The body is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroïn, melting-point 165° C. Yield quantitative.

Triphenylmethaneazometanitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2$-(*m*), is prepared by oxidation of the corresponding hydrazo-body. Recrystallized from methyl alcohol it forms canary-yellow needles.

0.2535 gram gave 22.5 cc. nitrogen at 23.5° and 734 mm.

	Calculated for $C_{25}H_{19}N_3O_2$.	Found.
N	10.67	9.98

The azo-compound is soluble in ether, benzene, less soluble in alcohol, and sparingly soluble in ligroïn, melting-point 111°–112° C. It forms a crystalline perbromide.

Triphenylmethaneazonitrobenzene, $C_{25}H_{19}N_3O_2 = 393$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
16.874	0.556	0.46°	361

Triphenylmethanehydrazoparanitrobenzene, $(C_6H_5)_3C.NH.NH.C_6H_4NO_2(p)$.—Paranitrophenylhydrazine[1] was allowed to act on triphenylbrommethane as in previous instances. The ethereal solution was evaporated nearly to dryness, when the hydrazo body crystallized in large reddish needles. Yield almost quantitative. Recrystallized from ether it gave the following figures:

0.2163 gram gave 21.8 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{25}H_{21}N_3O_2$.	Found.
N	10.63	11.15

Triphenylmethanehydrazoparanitrobenzene is very soluble in

[1] *Ber. d. chem. Ges.* **25**, 119, Ref.

benzene, chloroform and ether, less soluble in alcohol, and sparingly soluble in ligroïn. Melting-point 170° C. It is a weak base and forms salts with dry acids.

Triphenylmethaneazoparanitrobenzene, $(C_6H_5)_3C.N:N.C_6H_4NO_2$-(*p*).—This body results from the oxidation of the corresponding hydrazo-compound with amyl nitrite or nitrous acid gas, and crystallizes from methyl alcohol in large reddish needles. It was analyzed with the following results:

0.1763 gram gave 17 cc. nitrogen at 24° and 736.4 mm.

	Calculated for $C_{24}H_{19}N_3O_2$.	Found.
N	10.67	10.76

The compound is very soluble in benzene, chloroform, ether, less soluble in alcohol, and very sparingly in ligroïn. Melting-point 118.5° C. The determination of the molecular weight shows it to be monomolecular.

Triphenylmethaneazonitrobenzene, $C_{25}H_{19}N_3O_2 = 393$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
16.698	1.0965	0.855°	381

ACTION OF CHLORHYDRAZINES.

Metachlorphenylhydrazine, $ClC_6H_4.NHNH_2$.—Ten grams of metachloraniline were dissolved in ten times its weight of concentrated hydrochloric acid and cooled with ice. The calculated quantity of sodium nitrite, dissolved in twice its weight of water, was added. The diazo-solution was then reduced with the calculated quantity of stannous chloride dissolved in strong hydrochloric acid. A white precipitate of the double hydrochloride of tin and chlorphenylhydrazine separated out. This was redissolved in boiling water, decomposed with potassium hydroxide and the free base extracted with ether. The yield is about eighty-five per cent. of the theoretical quantity. Fractionated in a vacuum, it is obtained as a colorless liquid boiling at 165° C. at 23 mm. It remains liquid at —15° C. It gave the following figures on analysis:

0.2717 gram gave 0.2700 gram silver chloride.

0.1559 gram gave 27.7 cc. nitrogen at 23° and 739 mm.

	Calculated for $C_6H_7N_2Cl$.	Found.
Cl	24.91	24.55
N	19.65	20.19

Triphenylmethanehydrazometachlorbenzene, $(C_6H_5)_3C.NH.NH.C_6H_4Cl(m)$.—The preparation is similar to that of the preceding hydrazo-bodies. Recrystallized from ether it gave the following results on analysis:

0.3665 gram gave 23.8 cc. nitrogen at 21.5° and 737 mm.

	Calculated for $C_{25}H_{21}N_2Cl$.	Found.
N	7.28	7.36

It is colorless when pure, but turns yellow on exposure, due to partial oxidation. It is soluble in benzene, chloroform, less soluble in ether and alcohol, and very sparingly soluble in ligroïn. It melts at 150° C.

Triphenylmethaneazometachlorbenzene, $(C_6H_5)_3C.N:N.C_6H_4Cl(m)$.—This body is prepared in the same way as the previous azo-bodies. Recrystallized from methyl alcohol it forms bright yellow needles.

0.2607 gram gave 0.0632 gram silver chloride.

0.2463 gram gave 17 cc. nitrogen at 19° and 736.6 mm.

	Calculated for $C_{25}H_{19}N_2Cl$.	Found.
Cl	9.32	9.85
N	7.32	7.83

It is soluble in benzene, chloroform, less soluble in ether and alcohol, and is slightly soluble in ligroïn. It melts at 109° C. The following molecular weight determination shows it to be monomolecular.

Triphenylmethaneazochlorbenzene, $C_{25}H_{19}N_2Cl = 382.5$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.700	0.6452	0.475°	330

Trlphenylmethanehydrazoparachlorbenzene, $(C_6H_5)_3C.NH.NH.C_6H_4Cl(p)$.—This is obtained by the action of parachlorhydrazine on triphenylbrommethane. Analysis gave the following figures:

0.1593 gram gave 0.0715 gram silver chloride.

0.3458 gram gave 24.2 cc. nitrogen at 24° and 741.7 mm.

	Calculated for $C_{25}H_{21}N_2Cl$.	Found.
Cl	9.44	9.95
N	7.28	7.89

It melts at 145° C., and in other properties resembles the corresponding chlor-derivatives closely.

Triphenylmethaneazoparachlorbenzene, $(C_6H_5)_3C.N:N.C_6H_4Cl$-(*p*).—The preparation and properties of this body are similar to those of the corresponding chlorazo-body. It melts at 107° C.

0.142 gram heated to 130° C. gave 8.8 cc. nitrogen at 23.5° and 734 mm.

	Calculated for $C_{25}H_{19}N_2Cl$.	Found.
N	7.32	6.92

ACTION OF METABROMPHENYLHYDRAZINE.

Metabromphenylhydrazine, $C_6H_4Br.NHNH_2$.—This compound was prepared in the same way as the corresponding chlorhydrazine. It is a colorless liquid. Analyzed it gave the following results:

0.2672 gram gave 0.3687 gram carbon dioxide + 0.0942 gram of water.

0.1887 gram gave 25 cc. nitrogen at 21° and 746.8 mm.

0.4513 gram gave 58.4 cc. nitrogen at 18.5° and 727.7 mm.

	Calculated for $C_6H_7N_2Br$.	Found. I.	Found. II.
C	38.50	38.29	....
H	3.74	3.91	....
N	14.97	14.54	15.12

When the base is treated with hydrochloric acid a chloride containing one molecule of the acid is formed.

Triphenylmethanehydrazometabrombenzene, $(C_6H_5)_3C.NH.NH.$-C_6H_4Br(*m*).—Mode of preparation and properties similar to those of the corresponding chlor-compound; melting-point 149° C.

0.3017 gram gave 0.7693 gram carbon dioxide + 0.1336 gram of water.

0.3000 gram gave 18.8 cc. nitrogen at 19° and 741.7 mm.

0.2533 gram gave 16 cc. nitrogen at 22° and 734 mm.

	Calculated for $C_{25}H_{21}N_2Br$.	Found. I.	Found. II.
C	69.93	69.55	....
H	4.89	4.92	....
N	6.52	6.84	7.09

Triphenylmethaneazometabrombenzene, $(C_6H_5)_3C.N:N.C_6H_4Br$-(*m*).—Preparation and properties similar to those of the corresponding chlor-compound; melting-point 110° C. Analysis gave the following results:

0.2273 gram gave 0.5860 gram carbon dioxide + 0.1030 gram of water.

0.2606 gram gave 16.4 cc. nitrogen at 22° and 746 mm.

	Calculated for $C_{25}H_{19}N_2Br$.	Found.
C	70.25	70.31
H	4.45	4.85
N	6.55	6.92

Molecular weight determination:

Triphenylmethaneazobrombenzene, $C_{25}H_{19}N_2Br = 427$.

Solvent: Benzene.

Grams solvent.	Grams substance.	Observed depression.	Molecular weight found.
20.800	1.1020	0.70°	378

ACTION OF α-NAPHTHYLHYDRAZINE.

Triphenylmethanehydrazo-α-naphthalene, $(C_6H_5)_3C.NH.NH.C_{10}H_7$, is produced when triphenylbrommethane is treated with the α-naphthylhydrazine.[1] The ethereal solution should be evaporated in absence of air, and the crystalline residue rapidly dried, as this hydrazo-compound is very prone to oxidation, giving a dark-brown mass. The pure hydrazo-compound crystallizes in small white cubes.

0.2650 gram gave 18.2 cc. nitrogen at 21.5° and 734 mm.

	Calculated for $C_{29}H_{24}N_2$.	Found.
N	7.00	7.68

It is very soluble in ether, benzene, chloroform, less soluble in alcohol, and only slightly in ligroïn.

Triphenylmethaneazo-α-naphthalene, $(C_6H_5)_3C.N:N.C_{10}H_7(\alpha)$. —This azo-compound could not be obtained when amyl nitrite was employed. But upon careful oxidation of the hydrazo-derivative, suspended in a mixture of ether and ligroïn, with nitrous acid gas, the azo-body separates out in bright yellow needles, mixed with reddish-yellow cubes. Both forms of the crystals give the same melting-point, 114° C.

0.1995 gram gave 13.6 cc. nitrogen at 22° and 730 mm.

	Calculated for $C_{29}H_{22}N_2$.	Found.
N	7.03	7.61

In its general properties and solubility it resembles the other azo-derivatives of triphenylmethane.

ANN ARBOR, MICHIGAN.

1 *Ann. Chem.* (Liebig), **232**, 236.

A PERIODIDE OF TRIPHENYLBROMMETHANE.[1]

By M. Gomberg.

Received August 29, 1898.

In an attempt to prepare triphenyliodomethane the corresponding bromine compound was heated with finely powdered potassium iodide suspended in benzene. The solution soon turned dark red, showing the liberation of iodine from the potassium salt. The purer the bromine compound, the less iodine was set free, while prolonged boiling, even with the purest reagents, increased its yield. The benzene solution, filtered from the potassium salts, deposited, on cooling, a small crop of bluish green irridescent crystals, resembling, in their appearance and behavior, the well-known periodides of organic bases. The crystals contained both iodine and bromine, and it was therefore concluded that their formation was due to the action of the small quantity of free iodine upon the triphenylbrommethane.

Accordingly, a solution of iodine in benzene was added to a solution of the bromine compound, also in benzene. The periodide invariably separated in the form of crystals, the size of which depended upon the concentration of the solution. These crystals proved to be identical in every respect with those obtained when potassium iodide was employed.

The periodide was found to be of the composition

$$(C_6H_5)_3CBr.I_4,$$

with all the iodine held loosely, just as in the periodides of organic bases. The iodine could be titrated directly with standard solutions of sodium thiosulphate or sodium arsenite.

The periodide here described differs in some respects from the other compounds of this class. The formation of superiodides has been limited, with a few exceptions, to the nitrogen family of the elements,[2] the largest number of such superiodides being those of the organic nitrogen bases. Even the few exceptions are, after all, periodides of substances either themselves basic in their nature, or in combination with bases. The periodides of the diazo salts[3] are strictly such of bases. The superiodides of

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

[2] Prescott, *1895*: This Journal, 17, 779.

[3] Hantzsch, *1895*: *Ber. d. chem. Ges.*, 28, 27 4.

iodonium salts[1] find their explanation in the fact that the iodonium compounds are bases in every other respect as well. The periodides of metals are such of *inorganic* bases. The sulphon periodides of Kastle and Hill[2] are analogous to the herapathites of Jörgensen, with substitution of an inorganic base for an organic. The periodide of triphenylbrommethane, however, has not, so far as I am aware, its analogue. It is not a periodide of a salt of a base, nor of a free base[3]. On the contrary, triphenylbrommethane is made up entirely of negative groups. The periodide is unlike those recently described by Remsen and Norris.[4] It can hardly be assumed that the iodine adds itself to any of the benzene rings in the triphenylmethane. It must be linked to the molecule trough the bromine atom.

I have shown some time ago[5] that the amount of additive iodine (or bromine) in a base is in no way proportional to, or indicative of, the basic power of the compound. And here we have an example of a periodide, with as many as four atoms of additive iodine, of a substance which has no basic properties whatever.

Triphenylbrommethane Tetraiodide, $(C_6H_5)_3CBr.I_4$.—When a saturated benzene solution of iodine is added to a solution of triphenylbrommethane in benzene, a dark granular precipitate, soon changing to crystals, is thrown down. The periodide in this form always contains a little free iodine, which is difficult to remove by mere washing with benzene. When dilute solutions of the reagents are employed, the precipitation does not take place at once, and the solution has to be set aside for some time, or gently concentrated. Slow crystallization gives larger crystals, but these also contain frequently from two to three per cent. of free iodine. The periodide can also be obtained by substituting carbon disulphide for benzene, but in this case the solutions must be more concentrated, as the periodide is quite soluble in carbon disulphide. The amount of iodine employed varied in the different experiments from one-half to three times the theoretical quantity, but in no case was the formation

[1] *Ber. d. chem. Ges.*, **27**, 1594.
[2] *Am. Chem. J.*, **16**, 116.
[3] Such as $C_5N_5N.I_4$. (Prescott and Trowbridge: This Journal, **17**, 865.)
[4] *Am. Chem. J.*, **18**, 94, *1896*.
[5] This Journal, **18**, 377.

of either a higher or a lower periodide observed than the one here described. The yield is very good. When benzene is employed as a solvent, eighty to eighty-five per cent. of the theoretical quantity of the periodide is obtained.

For analysis, the periodide was recrystallized from warm benzene or carbon disulphide. The crystals were filtered off by means of a pump, washed with a little benzene, and dried, *in vacuo*, over sulphuric acid. The iodine was estimated in most cases by titrating weighed samples of the substance suspended in alcohol with a sodium thiosulphate solution. In some cases the iodine was estimated by reducing the periodide with zinc dust and water. The iodine was set free by a saturated solution of nitrous acid in concentrated sulphuric acid, extracted with carbon disulphide, the latter washed with a weak solution of sodium carbonate, and the iodine titrated as before. The bromine was estimated by igniting the periodide with lime and estimating the total halogen, *i. e.*, bromine and iodine together, with silver nitrate solutions. From the total mixture of silver halides, the quantity of silver iodide corresponding to the amount of iodine, as found by titration, is subtracted. The difference represents silver bromide.

The following are some of the analyses obtained on different samples of the perhalide :

I. 0.2203 gram substance gave 0.1340 gram iodine.
II. 0.3428 gram substance gave 0.2100 gram iodine.
III. 0.1641 gram substance gave 0.1027 gram iodine.
IV. 0.1495 gram substance gave 0.0914 gram iodine.
V. 0.2560 gram substance gave 0.1578 gram iodine.
VI. 0.4256 gram substance gave 0.2621 gram iodine.
0.2253 gram substance gave 0.3058 gram AgI.

	Calculated for $(C_6H_5)_3CBr.I_4$.	Found.					
		I.	II.	III.	IV.	V.	VI.
Iodine.....	61.05	60.83	61.26	62.58	61.50	61.64	61.58
Bromine ...	9.61	....	....	....	....	....	9.15

Estimation IV was done by previous reduction with zinc dust; all the others by direct titration.

The periodide is of a bluish-green iridescence. It can be obtained in long hexagonal prisms, or in small needle-like crystals. In two samples, obtained by slow crystallization, the crys-

tals were hollow, the canal coinciding as nearly as could be judged with the longitudinal axis of the crystals. The exact conditions necessary for the production of such hollow crystals have not been ascertained. Only two similar cases of crystallization have been reported, so far as I could find.[1] The periodide is only slightly soluble in cold benzene; more freely in hot. It is quite soluble in carbon disulphide. It is decomposed by alcohol and ether. When dry, and placed in a bottle, it remains unchanged for a long time; but when exposed to the air it gradually loses iodine. It melts at 121°–122° C.

A sample was gently heated at 40°–45° C. for some time, until the color changed to a dark gray. The residue was recrystallized from petroleum ether, and by its melting-point (152° C.) and all other properties was identified as bromtriphenylmethane.

Attempts to determine the molecular weight by the cryoscopic method did not give satisfactory results.

I wish to thank Mr. W. H. Hess, who kindly helped me in this work.

ANN ARBOR, MICHIGAN.

NITRIC NITROGEN PRODUCED BY THE PEA.

BY J. L. BESSON.

Received August 15, 1898.

IT has been long known that the leguminous plants contain more nitrogen than they get from the soil, hence their almost universal use as soil improvers.

Hellriegel and Wilfarth in 1886 showed that the leguminosæ would not grow in sterilized sand for lack of nitrogen, but that if the sand be inoculated with water, in which the roots of a well developed plant of the variety experimented on had been soaked, the plant would at once begin to grow, rapidly developing root tubercles. Microscopic investigation showed the presence of bacteria in these tubercles. These micro-organisms are now cultivated and sold under the name of "Nitragin" for the purpose of inoculating sterile soils, that is, soils which do not contain the leguminous micro-organisms.

Later experiments have shown that each kind of leguminous plant has its own kind of bacteria, and that those from another leguminous plant will not answer for inoculation purposes.

[1] Kebler, *1895*: *Am. J. Pharm.*, 67, 602: Trowbridge, *1897*: This Journal, 19, 328.

The bacteria live upon the juices of the host, and in turn supply the plant with nitric nitrogen assimilated from the air in the soil, thus establishing a symbiosis. While the roots of all the leguminosæ show rather large quantities of nitric nitrogen, the question whether these bacteria furnish all the plant needs or more, has not been determined, so far as I know. If the micro-organisms should produce more nitric nitrogen than the plant needs for its growth, will not this excess help to feed a crop growing among the leguminosæ? In order to answer these questions small plots of ground of uniform character were planted in peas, peas and corn, corn, cotton and sorghum, and one plot was cultivated like the planted plots, and kept free from vegetation. Since soils produce nitrates by nitrification, and by the fixation of nitrogen from the atmosphere by means of soil bacteria, this "fallow" plot was the zero point for the measurement of the nitric nitrogen in the soil of the plots that were planted.

The soil was a rich bottom land and very productive. The analyses were made September 30, after about six weeks of dry weather. This would allow the nitrates to accumulate, if formed in excess by the pea plants.

One kilogram of soil was taken about one foot from the plants, in several places, but towards the center of each plot. It was shaken for six hours with one liter of water, the suspended clay precipitated with five grams of sodium chloride, one-half liter decanted, evaporated to small bulk, and the nitric nitrogen estimated in duplicate by the Tiemann and Schulze method. The number of milligrams of nitric nitrogen in one kilo of soil is given for each plot below.

	Nitrogen. Mgms.
Fallow plot gave	1.01
Peas, growing, pods nearly grown	3.333
Peas, growing, pods about ripe	8.670
Peas, grown and dead two or three weeks	10.510
Corn (hard), peas same as above	7.503
Corn (hard)	0.340
Cotton, growing	0.423
Sorghum, growing	0.333

As was to be expected, practically no nitrates were found in

the soil under the growing cotton and sorghum. But more nitrates were found under the growing peas than under the fallow plot, showing that the micro-organisms on the pea roots assimilate more nitrogen than the plant needs for its growth, and that this excess is found in the soil. With the ripening of the peas the excess of nitrates increased, indicating a continuance of the activity of the micro-organisms until the plant has ceased to grow. It may be that they continue to grow and assimilate nitrogen after the pea plant is dead—as long as there are juices in the plant. The larger quantities of nitric nitrogen in the soil where the peas were dead, over that where the pods were ripe, would tend to show this. But the bacteriologist only can answer this question. The fact that the corn and peas plot showed less nitrates than the pea plot of the same age, yet more than the fallow plot, shows that the growing corn had used some of the nitrates in its growth. Had the corn been growing at the time the samples were taken, there would doubtless have been found still less nitrates, as the "corn" plot, though the corn was about dead, showed practically no nitrates. This excess of nitrates in the corn and pea plot was therefore likely produced largely after the corn had ceased to grow.

These experiments indicate that peas planted with a crop would tend to increase the yield of that crop, unless the peas be so thick as to interfere with the crop's root development, or use up too much water in their growth.

Whether these results will hold good for all leguminosæ, or for peas in all kinds of seasons, only further investigations can determine. It is to be hoped that the agricultural chemists of the various experiment stations will take up this very important line of work.

GEORGIA NORMAL AND INDUSTRIAL COLLEGE.

PETROLEUM INCLUSION IN QUARTZ CRYSTALS.[1]

BY CHAS. L. REESE.

Received August 29, 1898.

THE quartz crystals, of which an illustration is here given, are of interest on account of the size of the cavities and the quantity and character of the liquid in them.

[1] Read at the Boston meeting of the American Chemical Society, August, 1898.

Sir Humphry Davy,[1] in a study of the fluid contents of cavities in rocks, mentions a single instance in which mineral naphtha was found in a quartz cavity.

A. W. Wright[2] subjected smoky quartz from Branchville, Conn., to dry distillation, and obtained a bituminous material which probably came from microscopic cavities found in the crystals, and Foster[3] obtained a brownish liquid, which contained ammonium carbonate, by distilling smoky quartz.

I have had these crystals in my possession for a number of years and photographed them for the purpose of publishing an account of them, but have only recently been able to obtain definitely the locality from which they came. They were found at Diamond Post-Office, near Guntersville, Marshall Co., Alabama, near the Tennessee line.

The crystals are well developed, especially No. 2, and are perfectly transparent. No. 1 measures 23.6 mm. in length and twelve mm. in width, and No. 2 measures 13.5 mm. by 9.5 mm.

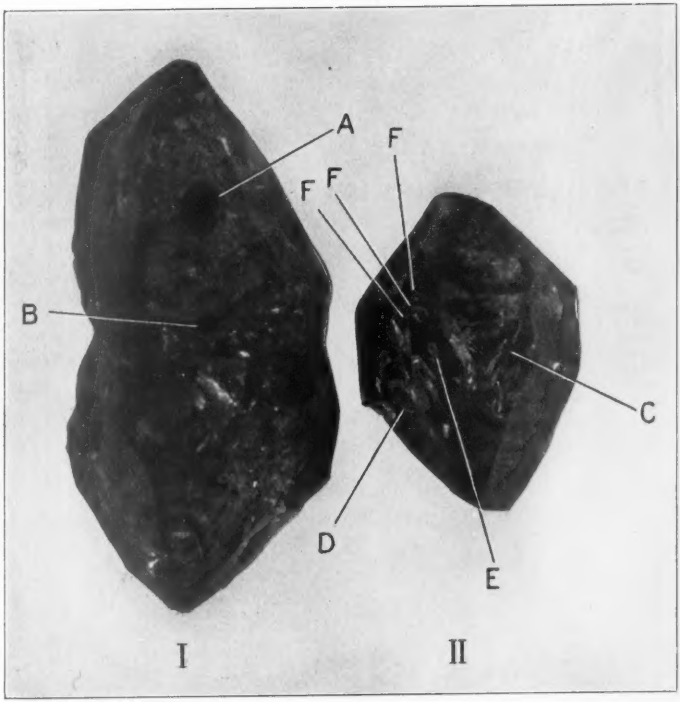
The globule in No. 1, marked *A*, measures two and three-tenths mm. through its longest diameter, by one and eight-tenths mm. through its shortest diameter, and about one mm. thick. The cavity in which *A* occurs is triangular in shape with sides and edges running parallel to the rhombohedral faces and edges and, as far as it can be measured, is about one millimeter deep; its sides measuring about six mm. by five mm. by five mm.

On heating No. 1, the globule *A* broke and the oil wet the sides and edges of the cavity so that it now lies about the walls of the cavity with a globular space in the center, and can be seen to move about when the crystal is turned from side to side. Globule *B* in No. 1 also broke when the crystal was heated and also spread itself about the cavity. The heating was done in water and the breaking of the globule was accompanied by quite an explosion, which caused my removing the crystal from the source of heat for fear of shattering the specimen.

There are other cavities in No. 1 containing oil, but they do not appear distinctly in the photograph.

In No. 2, the two larger cavities indicated in the figure by *C*

[1] *Phil. Trans.*, *1822*, 367.
[2] *Am. J. Sci.*, **21**, 209, *1881*.
[3] Pogg. *Ann.*, **143**, 173.


A
F
F
F
B
C
D
E
I
II

and *D*, are also triangular in shape, with edges parallel to the rhombohedral edges, and measure respectively, *C* four and five-tenths mm. by four and five-tenths by three mm., and for *D* three by three by two mm., both about five-tenths mm. thick.

These two cavities also contain oil with a globular space in the center, which can be seen to move about when the crystal is turned.

The cavities *E* and *F*, *F*, *F*, are quite small, but can be readily seen by the naked eye, and are full of oil with the exception of a minute globule of gas.

F, *F*, and *F* are the same cavity, being seen by refraction from the three faces.

The evidence of the character of the oil is not chemical, but yet sufficient to identify it.

It presents the appearance of petroleum in that it has the yellow green fluorescence. Some crystals from the same source were crushed in filter-paper, and the paper having absorbed the oil, showed the grease spot and gave the characteristic odor of petroleum and burned with a smoky flame.

Another evidence of the nature of the liquid is that petroleum occurs in the neighborhood where the crystals were found.

The specific gravity of crystal No. 2 is 2.6123.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 31.]

I. METAL SEPARATION BY MEANS OF HYDROBROMIC ACID GAS. II. INDIUM IN TUNGSTEN MINERALS.[1]

BY ELIZABETH ALLEN ATKINSON.

Received September 2, 1898.

INTRODUCTION.

THE application of hydrochloric acid gas as a means of separating metals has proved very successful. By means of this agent Moyer[2] volatilized the oxides of bismuth and antimony completely, separating bismuth from lead and copper, and antimony from copper and lead. In addition, this mode of analysis afforded him separations of arsenic from copper, lead, cadmium, silver, cobalt, and nickel.

[1] From author's thesis presented for the degree of Doctor of Philosophy.

[2] This Journal, 18, 1029: Thesis.

Hibbs[1] had previously separated arsenic acid from phosphoric acid and tungstic acid, as well as molybdic acid from phosphoric acid, while Smith and Meyer,[2] in studying the action of haloid acids in gas form upon the salts of the elements of Group V, had observed many interesting facts, of which some have already been utilized in effecting separations, while others still remain for development.

It is natural to suppose that in these cases, when hydrochloric acid has been shown to be an effective and satisfactory separating agent, if it be replaced by hydrobromic acid gas, or any haloid acid gas, the results can almost be predicted. However, experiment alone can demonstrate the correctness or falsity of this assumption. To that end the experiments recorded in the following pages were instituted and carried out along lines almost exactly like those followed by Moyer[3] in order that a fair comparison could be made.

Meyer and Smith[4] had noticed that hydrobromic acid gas expelled arsenic and vanadic acids from their salts. Kelley and Smith[5] found that arsenic in the form of sulphide was also decomposed and volatilized in an atmosphere of hydrobromic acid gas. Antimony sulphide behaved similarly. It would be interesting to subject other metallic sulphides to this reagent, for it is very probable that some of them would be volatilized as readily as happens when they are exposed to heated hydrochloric acid gas. In this latter way, Smith and Field[6] succeeded in separating arsenic from vanadium, thus obtaining a most accurate and satisfactory mode of separating these two metals.

I. METHOD OF WORK.

Hydrobromic acid gas was generated by dropping bromine from a separatory funnel on anthracene contained in a liter flask. Five drops a minute will give a good steady flow of the gas. The flask was placed on a water-bath in which the water was kept very near to the boiling-point.

The gas was passed through a tube containing anthracene, to

[1] This Journal, **17**, 682.
[2] *Ibid.*, **17**, 735.
[3] *Loc. cit.*
[4] *Loc. cit.*
[5] This Journal, **18**, 1096.
[6] *Ibid.*, **18**, 1051.

absorb any bromine that might be carried over, and then through a calcium-chloride tube, for absorption of moisture.

The substance to be acted upon was weighed out in a porcelain boat and placed in a combustion tube, which had been thoroughly dried. This tube was connected with the receiver by a bent tube provided with a stop-cock, which is necessary, as when the heat is removed there is danger of backward suction. The volatile substances were collected in water, with the exception of arsenic, in which case dilute nitric acid was used. The heat was obtained from a series of three fish-tail burners.

PREPARATION OF ANTIMONY TRIOXIDE.

Metallic antimony was ground in a mortar and treated with dilute nitric acid. The resulting metantimonic acid was dissolved in hydrochloric acid, and the oxychloride precipitated by an excess of water, washed thoroughly by decantation, dissolved in hydrochloric acid, and again precipitated. This procedure was repeated several times, and finally the antimony was precipitated by ammonium carbonate, filtered, washed, dried, and ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON ANTIMONY TRIOXIDE.

A slow current of the gas was passed over the oxide for one hour and a half. The first fifteen minutes in the cold; for an hour by heat given from a flame a half inch high, from three fish-tail burners placed two inches below the tube resting in an iron gutter.

At the end of the hour all the antimony had volatilized. The gas was then passed fifteen minutes in the cold, to insure the expulsion of all the volatilized bromide.

In the first experiments the tube containing the boat with the substance was run through holes in the ends of a drying oven. This oven was heated by means of a Bunsen burner. This method of heating had the advantage over that in which a direct flame was used, in that the exact temperature could be noticed by means of a thermometer.

After various experiments, I found it more satisfactory to be able to watch the reaction. The flow of gas and the heat could then be regulated so that the most satisfactory results could be obtained.

The volatilization of the antimony bromide could be somewhat hurried if a more rapid current of the gas was used, and a higher temperature allowed, but in view of the fact that this method was to be used as a means of separation from bromides of other metals that were slightly volatile at a high heat, I followed the above conditions.

PREPARATION OF LEAD OXIDE.

Pure lead acetate was ignited; the residue was dissolved in nitric acid, evaporated to dryness, and ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON LEAD OXIDE.

Hydrobromic acid gas was passed over the oxide for two hours, using a slightly higher temperature than with the antimony. The tubes were washed into the receiver and the tests made for lead. It was not present, proving that lead had not volatilized.

An amount by weight of the oxide was treated as above. After allowing it to cool in an atmosphere of the gas, the boat and its contents were removed to a desiccator, and after standing a half hour they were weighed.

The results indicated that the residue remaining in the boat was not lead bromide, but evidently a mixture of lead oxide and bromide. The boat and its contents were returned to the tube, and the reaction with the gas continued for one hour, when the boat was allowed to cool, and again weighed. It had gained in weight, indicating that more of the oxide had been changed into bromide. This led me to suppose that if the action of the gas was continued long enough all the oxide could be converted into bromide. This proved to be erroneous, as the weights taken after the substance had been exposed to the gas for four hours and for five hours were the same.

The following series of seven results seem to show that the compound obtained has the formula $PbO.5PbBr_2$:

Experiment.	PbO taken. Gram.	$PbO.5PbBr_2$ obtained. Gram.	$PbO.5PbBr_2$ required. Gram.	Difference. Gram.
1	0.1059	0.1626	0.1624	0.0002
2	0.1209	0.1862	0.1859	0.0003
3	0.1314	0.2029	0.2016	0.0013
4	0.1649	0.2534	0.2530	0.0004
5	0.2046	0.3150	0.3139	0.0011
6	0.1475	0.2270	0.2263	0.0007
7	0.1145	0.1747	0.1756	0.0009

Moyer's experiments with hydrochloric acid gas on lead oxide indicated that all the oxide changed completely into chloride, in the cold, in two hours, and that this chloride slightly volatilized at a temperature above 225°. His chloride completely dissolved in hot water. My compound, on treatment with hot water, left a small black residue.

THE SEPARATION OF ANTIMONY FROM LEAD.

The oxides were thoroughly mixed in a boat and the hydrobromic acid gas passed over them for one hour and a half. The same conditions were observed as when antimony was treated alone.

In experiments 1 and 2 the antimony was estimated as oxide; in the third experiment as sulphide.

Experiment.	Sb_2O_3 taken. Gram.	Sb_2O_3 found. Gram.	Difference. Gram.
1	0.1248	0.1248	0.0000
2	0.1042	0.1032	0.0012
3	0.1180	0.1174	0.0006

In the third experiment the treatment with the gas was continued until a constant weight was obtained for the residue in the boat. The compound which resulted corresponded to the formula $PbO.5PbBr_2$.

Experiment.	PbO taken. Gram.	$PbO.5PbBr_2$ obtained. Gram.	$PbO.5PbBr_2$ required. Gram.	Difference. Gram.
1	0.1180	0.1808	0.1813	0.0005

In the other two experiments compounds were obtained that did not even approximate any definite formula.

By this method a clean separation of antimony from lead may be effected.

PREPARATION OF BISMUTH OXIDE.

Commercially pure bismuth nitrate was dissolved in nitric acid and the oxynitrate precipitated by an excess of water, washed by decantation, filtered, dissolved in nitric acid, and reprecipitated by water. This operation was repeated several times. Finally the oxide was dissolved in nitric acid and precipitated with ammonium hydroxide and ammonium carbonate from a boiling solution. The basic carbonate, ignited to constant weight, gave pure bismuth trioxide.

ACTION OF HYDROBROMIC ACID GAS ON BISMUTH TRIOXIDE.

Hydrobromic acid gas was passed over a weighed amount of bismuth oxide for two hours and a half, the first thirty minutes in the cold; it was then gradually heated until the last half hour, during which time a flame was used from a fish-tail burner a half inch high, placed two inches below the tube.

The bismuth bromide was not so volatile as the antimony salt, but at the end of two hours and a half it was all volatilized if the above conditions had been observed. It first sublimed above the boat and could then be easily driven out of the tube.

The bismuth collected in the receiver was evaporated to dryness, taken up with nitric acid, and placed in a weighed crucible, when the solution was evaporated to dryness and taken up with nitric acid. This operation must be repeated several times, or the oxybromide which may be formed, is not entirely broken up. It was finally weighed as bismuth trioxide.

The following results were obtained:

Experiment.	Bi_2O_3 taken. Gram.	Bi_2O_3 found. Gram.	Difference. Gram.
1	0.1954	0.1954	0.0000
2	0.1575	0.1577	0.0002
3	0.1529	0.1534	0.0005

THE SEPARATION OF BISMUTH FROM LEAD.

The two oxides were thoroughly mixed in a porcelain boat. The hydrobromic acid gas was passed over them for two hours and a half. The same conditions were maintained as for the volatilization of the bismuth alone.

The following results were obtained:

Experiment.	Bi_2O_3 taken. Gram.	Bi_2O_3 found. Gram.	Difference. Gram.
1	0.1002	0.1006	0.0004
2	0.1356	0.1360	0.0004

The lead compound in the boat contained no bismuth, and the volatile sublimate showed, on appropriate tests, that lead was absent.

This separation cannot be carried out as rapidly as the separation of antimony from lead, owing to the less volatility of bismuth.

Moyer met difficulties in the separation of bismuth from lead by means of hydrochloric acid gas, owing to the fact that a little of the lead chloride volatilized at a temperature as low as 180°.

In the experiments with hydrobromic acid gas, I did not notice that any of the lead volatilized at a temperature necessary to volatilize the bismuth, but a slow current of the gas was best, as otherwise some of the lead was mechanically driven out with the bismuth.

Moyer found that it took from seven to eight hours to volatilize all of the bismuth by means of hydrochloric acid gas. My results show that it can be done with hydrobromic acid gas in two hours and a half.

The residue in the boat was weighed, but in no case did it correspond to a definite compound.

THE PREPARATION OF COPPER OXIDE.

Copper nitrate was recrystallized several times, and was then ignited to constant weight.

ACTION OF HYDROBROMIC ACID GAS ON COPPER OXIDE.

The hydrobromic acid gas was passed over the pure, black oxide for two and one-half hours, the same conditions being observed as with bismuth. On testing the contents of the receiver, copper was found to be absent.

SEPARATION OF BISMUTH FROM COPPER.

Pure bismuth oxide and copper oxide were weighed and thoroughly mixed, and then exposed to the action of hydrobromic acid gas for two and one-half hours. The conditions noted under bismuth were observed here.

The volatile bismuth bromide was collected in a receiver containing water and estimated by the method already described.

The copper compound remaining in the boat had various colors, always green when hot and usually grayish white when cold; but its weight, whatever its color, always corresponded to the formula CuBr. The compound held tenaciously to hydrobromic acid gas, so it was necessary to allow it to stand over soda-lime for at least forty-five minutes before weighing. The first few experiments gave varying results, because the heat used was too low, and the major part of the copper compound remained as cupric bromide in beautiful iodine-like crystals; but when sufficient heat was applied to volatilize all of the bismuth, the higher copper bromide was decomposed, the bromine coming off in clouds.

Moyer found that at the temperature necessary to volatilize bismuth chloride the cupric chloride was not decomposed, and that it could be weighed directly as that salt.

The following results were obtained, using this method of separation:

Experiment.	Bi_2O_3 taken.	Bi_2O_3 found.	Difference.
	Gram.	Gram.	Gram.
1	0.1273	0.1277	0.0004
2	0.1111	0.1121	0.0010
3	0.1162	0.1170	0.0008

Experiment.	CuO taken.	CuBr found.	CuBr required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1103	0.2010	0.1996	0.0014
2	0.1318	0.2385	0.2394	0.0009

SEPARATION OF ANTIMONY FROM COPPER.

The same material was used as in the preceding experiments. The weighed oxides were thoroughly mixed. The antimony bromide was completely volatilized in one and a half hours, leaving cuprous bromide in the boat. The same care was exercised as in the separation of bismuth from copper, to insure the decomposition of the cupric bromide to cuprous bromide.

The volatile antimony bromide was collected in water.

At the close of the reaction the tubes and bulb were washed out with acidulated water, and the antimony precipitated with hydrogen sulphide water. The antimony sulphide was then fil-

tered through a tared filter, the precipitate washed with alcohol, with carbon disulphide, again with alcohol, and finally with a mixture of alcohol and ether. It was then dried at from 105° to 110° in the air-bath, and weighed. The copper was weighed as cuprous bromide.

This bromide, as before mentioned, had various colors, running from a light gray through yellow and green to almost a black.

The copper bromide obtained contained no antimony, and the volatile antimony compound was entirely free from copper.

Experiment.	CuO taken. Gram.	CuBr found. Gram.	CuBr required. Gram.	Difference. Gram.
1	0.1025	0.1853	0.1855	0.0002
2	0.1218	0.2210	0.2204	0.0006
3	0.1137	0.2059	0.2058	0.0001

Experiment.	Sb_2O_3 taken. Gram.	Sb_2S_3 found. Gram.	Sb_2S_3 required. Gram.	Difference. Gram.
1	0.1250	0.1465	0.1458	0.0007
2	0.1181	0.1385	0.1377	0.0008

PREPARATION OF COPPER ARSENATE.

Commercial, chemically pure sodium arsenate was recrystallized three times and then gently ignited for one hour. Pyroarsenate resulted. Copper sulphate was recrystallized three times. A solution of this salt was mixed with a solution of the pure pyroarsenate, when green copper arsenate was precipitated. It was washed repeatedly and dried in an air-bath at 100°.

Salkowski[1] states that copper arsenate still contains water above 130°. Moyer worked with a salt with the composition $Cu_3As_2O_8.2H_2O$. My salt prepared by the same method had the same composition.

SEPARATION OF ARSENIC FROM COPPER.

The weighed copper arsenate was exposed to the action of the hydrobromic acid gas for two hours—fifteen minutes in the cold, one hour with the flame of three fish-tail burners a quarter of an inch high, a half an hour with flame an inch high from the same burners, and finally fifteen minutes in the cold.

The arsenic and water were driven out at the low heat. Higher heat decomposed the cupric bromide into cuprous bro-

[1] *J. prakt. Chem.*, 104, 124.

mide and bromine. The cuprous bromide may be weighed in that condition after it has stood over soda-lime for forty-five minutes. Its color varied as it did in the other experiments already described.

The arsenic was washed out of the bulb into a beaker, warmed with nitric acid to insure oxidation, and precipitated from an ammoniacal solution with a magnesium solution. It was finally weighed as magnesium pyroarsenate.

The results follow :

Experiment.	$Cu_2As_2O_8 + 2H_2O$ taken.	CuBr obtained.	CuBr required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1227	0.1054	0.1046	0.0008
2	0.1238	0.1051	0.1055	0.0004
3	0.1137	0.0958	0.0969	0.0011

Experiment.	$Cu_2As_2O_8 + 2H_2O$ taken.	$Mg_2As_2O_7$ obtained.	$Mg_2As_2O_7$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1238	0.0766	0.0762	0.0004

PREPARATION OF SILVER ARSENATE.

The pure sodium pyroarsenate prepared as before described, was precipitated with silver nitrate. The nitrate was kept in excess. The reddish brown precipitate was washed with boiling water until the filtrate ceased to show the presence of silver when tested with hydrochloric acid. The silver arsenate was dried at 110°.

SEPARATION OF ARSENIC FROM SILVER.

Hydrobromic acid gas attacked the silver arsenate in the cold, forming yellow silver bromide. In the following experiments the salt was exposed to the action of the gas for one hour and a quarter. The reaction was allowed to take place for a half hour in the cold, and for thirty minutes a low heat was used. The resulting bromide was allowed to cool in the gas. Silver was not present in the receiver, and the silver bromide also proved to be free from arsenic.

The silver bromide was weighed as such. The arsenic was estimated as magnesium pyroarsenate.

Experiment.	Ag_3AsO_4 taken.	AgBr obtained.	AgBr required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1783	0.2174	0.2171	0.0003
2	0.1990	0.2429	0.2424	0.0005
3	0.1677	0.2050	0.2042	0.0008

Experiment.	Ag_3AsO_4 taken.	$Mg_2As_2O_7$ obtained.	$Mg_2As_2O_7$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1677	0.0561	0.0561	0.0000

PREPARATION OF CADMIUM ARSENATE.

Cadmium sulphate was recrystallized three times and then precipitated by a solution of sodium pyroarsenate. A white gelatinous salt was precipitated, which, upon stirring, became granular. The salt was washed thoroughly and dried at 110°.

Salkowski[1] had previously prepared this salt and observed that a red heat was necessary to completely dehydrate it. Moyer's salt contained two molecules of water. My salt also had the composition $Cd_2As_2O_8 + 2H_2O$.

SEPARATION OF ARSENIC FROM CADMIUM.

The hydrobromic acid gas was passed over the arsenate for one hour and a half, the same conditions being maintained as for the silver arsenate. The arsenic in the receiver showed no trace of cadmium. The cadmium in the boat was transformed into the white bromide, and was free from arsenic. It was weighed as cadmium bromide. The arsenic was determined as magnesium pyroarsenate.

Experiment.	$Cd_2As_2O_8 + 2H_2O$ taken.	$CdBr_2$ obtained.	$CdBr_2$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1041	0.1294	0.1306	0.0012
2	0.1104	0.1378	0.1385	0.0007
3	0.1168	0.1471	0.1472	0.0001

Experiment.	$Cd_2As_2O_8+2H_2O$ taken.	$Mg_2As_2O_7$ obtained.	$Mg_2As_2O_7$ required.	Difference.
	Gram.	Gram.	Gram.	Gram.
1	0.1041	0.0485	0.0494	0.0009

PREPARATION OF COBALT ARSENATE.

A solution of pure cobalt nitrate was precipitated by a solution of pure sodium pyroarsenate. The purplish-pink salt having the formula $Co_2As_2O_8 + 2H_2O$ was precipitated. It was

[1] *Loc. cit.*

thoroughly washed by decantation, and then gently ignited, until its weight was constant; the blue, anhydrous salt resulted.

SEPARATION OF ARSENIC FROM COBALT.

The hydrobromic acid gas attacks the cobalt arsenate in the cold, but the reaction takes place sooner if a low heat is applied. The blue arsenate is changed first to a pink bromide; this, on the application of heat changed to a dark green, anhydrous bromide. The low heat of 130° volatilized all the arsenic, leaving all of the cobalt in the boat. The arsenic was estimated in the usual manner.

The boat with its contents, after being cooled in a current of hydrobromic acid gas, and then standing in a desiccator for fifteen minutes, was weighed. Notwithstanding that it absorbs water rapidly, the weight was low if it was calculated as cobalt bromide.

In the first experiment the material taken was 0.1384 gram, the compound weighed 0.1640 gram. If the cobalt compound were cobalt bromide, it should weigh 0.2002 gram. The weight of the compound obtained, 0.1640 gram, is eighty-nine per cent. of the weight required.

In the second experiment, the cobalt arsenate taken was 0.1382 gram; the compound obtained weighed 0.1630 gram. If the cobalt compound were cobalt bromide it should have weighed 0.1999 gram. The weight of the compound obtained, 0.1630 gram, is only 81.5 per cent. of the required weight.

These results led to the conclusion that an oxybromide of indefinite composition is formed.

The next step was to heat the cobalt bromide in a stream of hydrogen, obtaining the metal.

The following satisfactory results were obtained:

Experiment.	$Co_3As_2O_8$ taken. Gram.	Co obtained. Gram.	Co required. Gram.	Difference. Gram.
1	0.1382	0.0525	0.0531	0.0006
2	0.1244	0.0475	0.0478	0.0003
3	0.1228	0.0473	0.0472	0.0001

Experiment.	$Co_3As_2O_8$ taken. Gram.	$Mg_3As_2O_7$ obtained. Gram.	$Mg_3As_2O_7$ required. Gram.	Difference. Gram.
1	0.1384	0.0943	0.0949	0.0006
2	0.1382	0.0945	0.0947	0.0002

PREPARATION OF IRON ARSENATE.

Chemically pure ferrous ammonium sulphate was dissolved in water and oxidized with nitric acid, and the ferric salt was crystallized from the solution. The best crystals were dissolved in water and precipitated by a solution of pure sodium pyroarsenate. The yellowish precipitate was washed by decantation, filtered, and the washing continued until the filtrate gave no precipitate with potassium ferrocyanide. The salt was then dried and gently ignited. It is necessary that this ignition should be carefully carried out, as there is danger of decomposing the salt.

SEPARATION OF ARSENIC FROM IRON.

The results were unsatisfactory. The acid gas acted very energetically on the arsenate. Even in the cold the bromide formed creeps over the sides of the boat, its contents becoming a reddish brown liquid. Unless the current of gas is very slow, and the heat applied very gently, the contents will spatter. The final product was a beautiful red compound, which took up water rapidly. It was dissolved in hydrochloric acid, oxidized with nitric acid, and the iron precipitated with ammonia. Several experiments were carried out; in every case the iron content was low. I was unable to account for this loss, as there was no iron present with the volatile arsenic in the receiver. The residue in the boat was free from arsenic.

BEHAVIOR OF MINERALS IN HYDROBROMIC ACID GAS.

Galenite.—A weighed amount of the mineral was placed in the boat and exposed to the action of the hydrobromic acid gas for two hours. For one hour of the time a temperature of 100° was maintained. Before the heat was applied hydrogen sulphide was evolved. After heating, the antimony in the galenite was volatilized and carried over into the receiver, where it was precipitated by the hydrogen sulphide that had been collected in the water, as the orange-colored sulphide of antimony. Tests were applied to the residue in the boat, and it was found to be free from antimony. The volatile products showed no lead, indicating a method for the decomposition and estimation of mineral sulphides that may prove more satisfactory than the present, often tedious, processes.

Smith and Hibbs[1] previous to this have shown that mimetite loses its arsenic quantitatively when heated in a stream of hydrochloric acid gas. Moyer found in his investigation that niccolite, exposed to the action of hydrochloric acid gas, was only slightly affected. If the niccolite was first dissolved in nitric acid and after evaporation to dryness, exposed to the gas, it was completely decomposed, giving a quantitative separation of the arsenic from the nickel.

SUMMARY.

A comparison of the results obtained in separating metals by means of hydrobromic acid gas, and those resulting through the action of hydrochloric acid gas, leads to the conclusion that those metals thus far studied that are volatile in one gas are volatile in the other, and that the same separations may be effected. The principal difference lies in the length of time which is required to make a separation.

The chlorides of antimony and bismuth require from six to eight hours for their complete volatilization. Antimony bromide can be entirely driven out in one hour and a half. The bismuth requires about an hour longer. In the case of arsenic, both the chloride and the bromide are volatilized in an hour and a half.

Some of those metals which do not form volatile compounds with the respective gases, have a tendency in the case of hydrobromic acid, to form oxybromides ; the lead compound approximating the formula $PbO.5PbBr_2$, while the lead chloride can be weighed directly as $PbCl_2$. Cobalt also forms an oxybromide, while the chloride compound is probably free from oxygen.

After the reaction is finished between the hydrobromic acid gas and copper, cuprous bromide is the result ; in the case of hydrochloric acid gas it remains as the cupric compound.

Silver is changed to the chloride and bromide by the action of the respective gases. Cadmium is also changed to a non-volatile chloride and bromide.

Unsatisfactory results were obtained by the use of both reagents in an attempt to separate arsenic from iron.

[1] *Loc. cit.*

II. INDIUM IN TUNGSTEN MINERALS.

It was about the year 1866 that Hoppe-Seyler,[1] while engaged in the analysis of wolframite from Zinnwald, discovered that indium was present in it.

He obtained 0.028 gram of indium from 122.6 grams of the mineral. He believed that as the latter contained zinc, the indium was probably present in the zinc blende, inasmuch as the quantity of indium found by him was not very much greater than that contained in Freiberg zinc blende. Thinking that indium might possibly be a constant, regular constituent of tungsten-bearing minerals, I resolved to examine some of the latter for this interesting ingredient. The results are appended.

WOLFRAMITE FROM ZINNWALD.

Three hundred grams of wolframite from Zinnwald were ground and then treated with aqua regia. Several days were required for the complete decomposition of the mineral. The acid solution was then evaporated to dryness, and the residue moistened with dilute hydrochloric acid and taken up with water. The acid was neutralized with sodium carbonate; sodium acetate and a few drops of acetic acid were added. Hydrogen sulphide was then passed through this solution until it was thoroughly saturated with the gas. A yellowish brown precipitate at first came down, soon followed by a black precipitate. These were filtered, redissolved in hydrochloric acid, and the treatment outlined above repeated. It was found necessary to repeat several times before a pure yellow precipitate was obtained.

This yellow compound was dissolved in hydrochloric acid and when examined with the spectroscope gave the bright blue line of indium. The hydrochloric acid solution, upon treatment with ammonium hydroxide, precipitated a white gelatinous mass. This was filtered, dried, and ignited, when a yellow residue remained, which was the oxide of indium. Its weight was 0.0145 gram.

The filtrate from the indium hydroxide was evaporated to a small bulk, and treated with ammonium hydroxide. The solution was bright blue, and on treatment with ammonium sulphide

[1] *Ann. Chem.* (Liebig), 140, 247.

gave a grayish, chocolate-colored precipitate. This all dissolved in dilute hydrochloric acid, with the exception of a black sediment. A copper bead was obtained with this insoluble portion.

Hydrogen sulphide when passed through the filtrate gave no precipitate, but after neutralizing with ammonium hydroxide and adding ammonium sulphide, a dirty white precipitate came down. This gave Rinman's green, an evidence of zinc.

WOLFRAMITE FROM CORNWALL, ENGLAND.

The mineral was an impure specimen. After it was broken into small pieces, the purest portions were ground up, and 300 grams were treated with aqua regia. The solution was poured off, the mineral again treated with acid, and the solution added to the first one. This treatment was continued until all of the mineral was decomposed.

The aqua regia solution was evaporated to dryness, taken up with hydrochloric acid and water, and after neutralization with sodium carbonate and addition of sodium acetate and acetic acid, was treated with hydrogen sulphide gas. The precipitate obtained was reddish brown in color. It dissolved in hydrochloric acid. When examined with the spectroscope, indium could not be discovered.

The hydrochloric acid solution was then examined as under the Zinnwald wolframite, but no zinc could be detected.

HÜBNERITE FROM COLORADO.

One hundred and fifty grams of hübnerite from Colorado were treated with aqua regia, and the further treatment for the isolation of indium, as already outlined, was carried out. Hydrogen sulphide caused a reddish precipitate, which dissolved in hydrochloric acid, and proved not to be indium. Zinc was also absent.

SCHEELITE FROM NEW ZEALAND.

Two hundred and fifty grams of this mineral were decomposed with aqua regia. There resulted the usual reddish precipitate with hydrogen sulphide in the acetate solution.

The hydrochloric acid solution when tested with the spectroscope gave a blue line, which at first was thought to be the

indium line; but on closer examination it proved to be the strontium line. The indium and strontium lines lie close together. The line which I found had a wave-length of 4.61×10^{-5}, corresponding to the line Srρ; whereas the indium lines are In_{α} 4.51×10^{-5} and In_{β} 4.10×10^{-5}.

The acid solution, neutralized with sodium carbonate, gave a white precipitate; on drying, a yellow powder was obtained, which proved to be calcium corbonate. Zinc was not present.

SCHEELITE FROM BOHEMIA.

A pure specimen of this mineral was subjected to the same treatment as has been described. The same results were obtained. No indium could be detected and the absence of zinc was proved.

The care exercised in the selection of material, and the large quantities employed, while working with every precaution, would seem to justify the conclusion that indium cannot be regarded as an associate of tungsten in its natural derivatives; that most probably the suspicion of Hoppe-Seyler in regard to its origin, *viz.*, blende, is correct, for it was only in the Zinnwald specimen that I could detect it.

UNIVERSITY OF PENNSYLVANIA.

NEW BOOKS.

EXPLOSIVE MATERIALS. The Phenomena and Theories of Explosion and the Classification, Constitution, and Preparation of Explosives. By 1ST LIEUT. JOHN P. WISSER, 1st Art., U. S. A. New York: D. Van Nostrand Company. 1898. Price, 50 cents.

This little book, which is issued as No. 70 in Van Nostrand's Science Series, bears the same leading title as the No. 70 of this series issued in 1883, but, while the contents of the 1883 edition consisted of a translation of "Berthelot's Lecture on Explosive Materials" by Dr. Marcus Benjamin, a translation of "Braun's Historical Sketch of Gunpowder" by Lieut. John P. Wisser, and a "Bibliography of Works on Explosives" by W. H. Farrington, the present edition contains an original essay by Lieut. Wisser only, which is based upon the lecture of Berthelot, but, which includes the more recently adopted theories, and much descriptive matter. Where considerable space is given to the display of graphic formulas of substances used in the manu-

facture of explosive materials, it is obviously impossible to give any lengthy descriptions of processes of manufacture in 145 small pages of a pocket volume, such as this is, yet the author has contrived to put a very large amount of reliable information between its covers, and his descriptions, though brief, are clear and accurate. It is greatly to be regretted that the publishers have not done their part as well as the author has done his, and that the volume should be marred by typographical errors while its general make-up is quite unattractive. Nevertheless the book may be recommended as a useful one to keep at hand as a ready reference work on this important subject.

CHARLES E. MUNROE.

BOOKS RECEIVED.

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